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Removal of Nitrate from Contaminated Water Supplies for Public Use

Boyle Engineering Corp.
Bakersfield, CA

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February 1981

REMOVAL OF NITRATE FROM CONTAMINATED WATER SUPPLIES FOR PUBLIC USE

INTERIM REPORT

by

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EPA Grant No. R-805900-01

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16. ABSTRACT

This research program has the objective to evaluate the general applicability of three treatment processes for removal of nitrate from public water supplies. The processes are reverse osmosis (R.O.), ion exchange, and the combination of R.O. followed by ion exchange. The evaluation consists of using laboratory size and field-test equipment to establish design criteria and operating experience useful for designing a full-scale plant of approximately 1 mgd capacity.

The program was conducted by the McFarland Mutual Water Co. (McMWCo) at Well 3 in McFarland, California. Ion exchange column tests were conducted with five strong-base anion exchange resins on nitrate-laden waters of various anion compositions. From this work, estimates of product water quality and the bed volume capacity for feedwater of any composition can be made. Also, a working hypothesis was developed from an analysis of the data about how the chemical structure of resins can be practically altered to obtain nitrate selectivity.

A 20-inch-diameter pilot anion exchange column was designed and operated for over one year at Well 3. The column contained 4.36 cubic feet of resin. Data from this column operation is used to verify estimates of pilot column performance and to project the cost for equipment and regenerant for a well site installation to treat up to 1 mgd. Because of the interim nature of this report, only preliminary data is reported on the operation of a 20,000-gallon per day R.O. system.

This interim report is the seventh of a series of quarterly progress reports in fulfillment of a contract under Environmental Protection Agency Grant R-805900-01 to the McMWCo of McFarland, California. This report covers work from July, 1978, to April 1, 1980, with emphasis on the ion exchange process. The reader should be aware that ion exchange experiments are being continued under this program and could alter conclusions concerning cost of the ion exchange process reported herein.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

The pollution of our nation's groundwater has been called the environmental problem of the 1980s. When polluted groundwater serves as a source of public drinking water, pollutants must be removed to levels below standards regulated by the Safe Drinking Water Act (Public Law 93-523). Nitrate is one of the pollutants frequently found in groundwater used for drinking water supplies and is the cause of serious and occasionally fatal poisonings in infants. This report summarizes studies being conducted in behalf of small communities on processes for removal of nitrate from groundwater supplies.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

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An experimental program was conducted using both laboratory size and pilot scale equipment. The program was conducted by the McFarland Mutual Water Co. (McMWCo) at Well 3 in McFarland, California. Ion exchange column tests were conducted with five strong-base anion exchange resins on nitrate-laden waters of various anion compositions. From this work, estimates of product water quality and the bed volume capacity for feedwater of any composition can be made. Also, a working hypothesis was developed from an analysis of the data about how the chemical structure of resins can be practically altered to obtain nitrate selectivity.

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LIST OF ABBREVIATIONS AND SYMBOLS

α_{Cl}^{N}	--	Separation factor indicating relative preference of resin for nitrate over chloride.
α_{N}^{S}	--	Separation factor indicating preference of resin for sulfate over nitrate.
A-F	--	Volume of water, acre-foot.
APHA	--	American Public Health Association.
BV	--	Bed volume. Relative volume of water compared to volume of ion exchange bed.
BV(N)	--	The number of bed volumes of water treated to reach nitrate breakthrough.
BV(N)'	--	Bed volumes of water which can be treated until nitrate breakthrough is reached using an incompletely regenerated resin.
C	--	Sum of anion equivalents in solution.
$\overline{C}$	--	Exchange capacity of resin, usually expressed in ionic equivalents per liter of resin.
ca	--	"circa" meaning approximately.
$\overline{Cl}$	--	Chloride ions in resin phase.
cfm	--	Flow rate, cubic feet per minute.
EPA	--	Environmental Protection Agency.
eq	--	Equivalent.
f	--	Fraction of ion exchange bed.
gpm	--	Flow rate, gallons per minute.
ID	--	Inside diameter of pipe.
K_{Cl}^{N}	--	Selectivity coefficient indicating selectivity of resin for nitrate relative to chloride.

K_N^S	--	Selectivity coefficient indicating selectivity of resin for sulfate relative to nitrate.
McMWCo	--	McFarland Mutual Water Co.
mgd	--	Flow rate, million gallons per day.
meq	--	Milliequivalent.
mg/l	--	Concentration of substance in water, milligrams of substance per liter of water.
ml	--	Milliliter.
$\overline{NO_3}$	--	Nitrate ions in resin phase.
ppm	--	Concentration of a substance in water, parts by weight of substance per million parts by weight of water.
PVC	--	Polyvinyl chloride.
R.O.	--	Reverse osmosis.
$\overline{SO_4}$	--	Sulfate ions in resin phase.
TDS	--	Total quantity of dissolved substance in water. Commonly used to refer to amount of inorganic salts dissolved in water.
X_N	--	Equivalent fraction of nitrate ions in solution.
$\overline{X_N}$	--	Equivalent fraction of nitrate ion on resin.
$\overline{X'_N}$	--	Equivalent fraction of nitrate ion in nonsulfate portions of resin.
X_s	--	Equivalent fraction of sulfate ion in solution.
$\overline{X_s}$	--	Equivalent fraction of sulfate ion on resin.

ION EXCHANGE CONVERSION TABLES

VOLUME

	Cu Ft	Gal (U.S.)	Gal (Imp.)	Liters	Cu Meters
1 cu ft	1	7.48	6.23	28.3	0.0283
1 gal (U.S.)	0.134	1	0.833	3.785	0.003785
1 gal (Imp.)	0.160	1.2	1	4.53	0.00453
1 liter	0.353	0.264	0.220	1	0.001
1 cu meter	35.3	264	220	1,000	1

MASS

	Pounds	Grams	Kilograms	Grains	Kilograins
1 lb	1	453.6	0.4536	7,000	7
1 gram	0.0022	1	0.001	15.43	0.01543
1 kilogram	2.2	1,000	1	15,430	15.43
1 grain	0.000143	0.065	0.000065	1	0.001
1 kilograin	0.143	65	0.065	1,000	1

DENSITY

	Lb/ Cu Ft	Grams/ Liter	Lb/Gal (U.S.)	Lb/Gal (Imp.)
1 lb/cu ft	1	16	0.134	0.160
1 gram/l	0.0624	1	0.00834	0.010
1 lb/gal (U.S.)	7.48	120	1	1.2
1 lb/gal (Imp.)	6.24	100	0.834	1

FLOW RATE*

	BV/ Min	Gal (U.S.)/ Cu Ft/Min	Gal (Imp.)/ Cu Ft/Min	Lb H_2O/ Cu Ft/Min
1 BV/min	1	7.48	6.24	62.4
1 gal (U.S.)/cu ft/min	0.134	1	0.833	8.33
1 gal (Imp.)/cu ft/min	0.161	1.20	1	10
1 lb H_2O cu ft/min	0.016	0.12	0.10	1

*To convert flow rate per volume to flow rate per unit area, multiply flow rate per unit volume by resin volume, and divide by cross-sectional area.

WATER CONVERSION TABLE*

1 cubic foot . . . . . 7.48 gallons . . . . . 62.4 pounds of water

1 acre-foot . . . . . 43,560 cubic feet . . . . . 325,900 gallons

An acre-foot covers 1 acre of land 1 foot deep

1 cubic foot per second (cfs) . . . . . 450 gallons per minute

1 cfs . . . . . 646,320 gallons per day

For 24 hours . . . . . 1.983 acre-feet

For 30 days . . . . . 59.5 acre-feet

For 1 year . . . . . 724 acre-feet

1 million gallons . . . . . 3.07 acre-feet

1 million gallons per day (mgd) . . . . . 1,120 acre-feet per year

1,000 gallons per minute (gpm) . . . . . 2.23 cfs

1,000 gpm . . . . . 4.42 acre-feet per day

At 10 cents per 1,000 gallons . . . . . $32.59 per acre-foot

*Approximate values.

SECTION 1

INTRODUCTION

SCOPE OF REPORT

The purpose of the work done under this grant is to objectively evaluate the general applicability of three treatment processes for removal of nitrate from public water supplies. The processes are reverse osmosis (R.O.), ion exchange, and the combination of R.O. followed by ion exchange. Both laboratory-size and field-test equipment are being used to establish design criteria and operating experience useful for designing full-scale plants of approximately 1-million gallon per day (mgd)* capacity.

This special report summarizes all work done during the period July, 1978, to April, 1980, with emphasis on the ion exchange process. Work is continuing on ion exchange and R.O. The remainder of the work will be reported in the final report under this grant.

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*List of Abbreviations and Symbols is on pages xi and xii, and Conversion Tables are on pages xiii and xiv.

CONCLUSIONS

Engineering Aspects

1. Design parameters for application of a conventional single bed ion exchange process with downflow regeneration for removal of nitrate from well waters have been developed and tested using laboratory columns and a 20-inch-diameter pilot column. The process is depicted in Figure 1 for a well water of moderate nitrate and sulfate levels. Pilot column tests were conducted using a Type I strong base anion exchange resin at Well 3 in McFarland, California. Well 3 is high in nitrate (ca 90 parts per million [ppm]) and sulfate (ca 320 ppm), making it a useful research well. Modifications were made to a conventional automatic water softener to convert it to the 20-inch anion exchanger pilot column.

2. The study indicates that automatic ion exchange equipment, which is commonly used by the water softening industry, can be adapted for nitrate removal. The equipment can be installed at a well site for direct treatment of well water and operated on demand without storage.

3. The selected resin was effective for nitrate removal for flow rates over 20 gallons per minute (gpm) per square foot of bed area (1.38 bed volumes [BV] per minute). This was near the upper limit of the test equipment used. These high flow rates bring the cost of capital equipment and resin quantities to low practical levels.

4. Capital equipment costs of an ion exchange system for treating one-half of a 1-mgd production well are estimated to be less than $90,000 installed. This estimate is based on moderate nitrate levels of less than 60 ppm in well water and sulfate levels less than 200 ppm and blending of

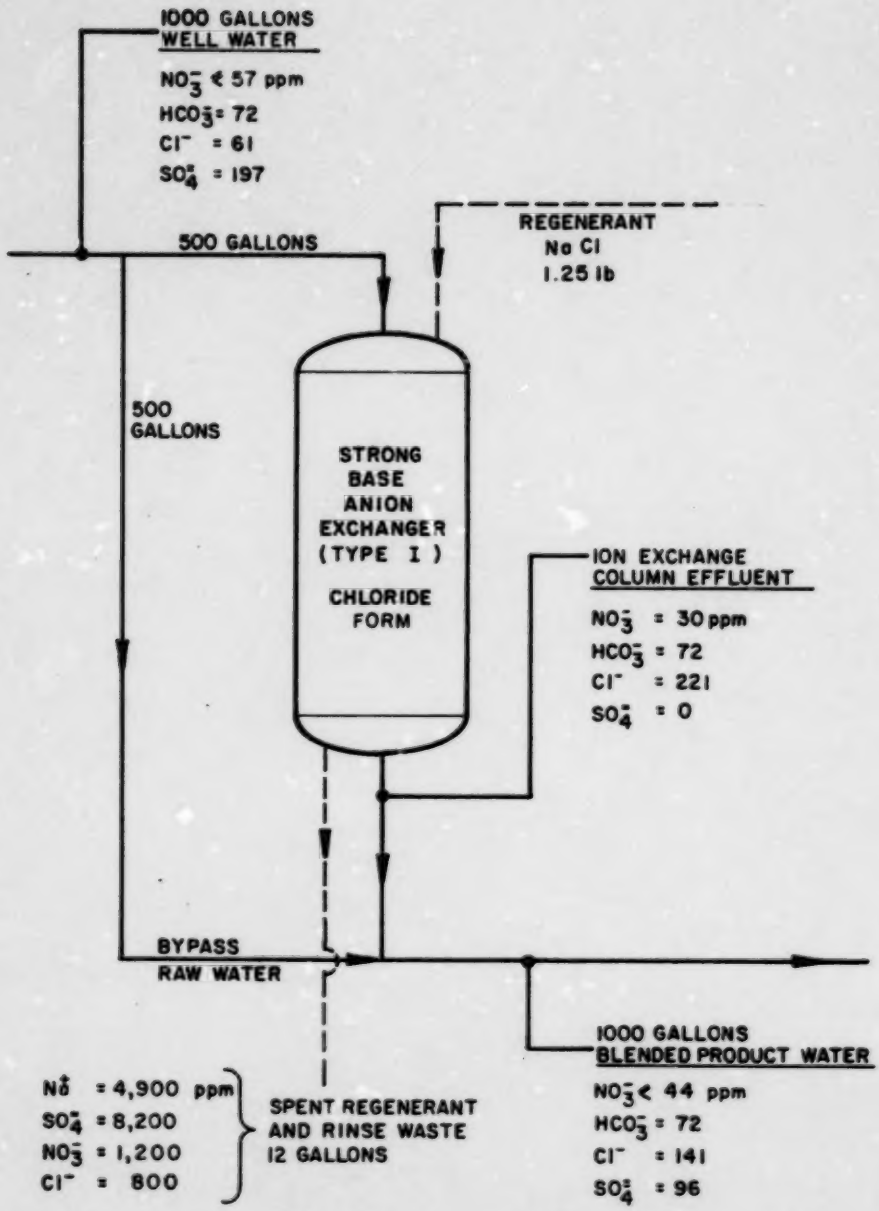

FIGURE I. CONVENTIONAL SINGLE BED ION EXCHANGE PROCESS

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treated with raw water to produce a water less than 45-ppm nitrate (see Figure 1).

The corresponding equipment cost estimate for a system to treat all water from a 1-mgd production well is less than $150,000. This is based on high nitrate levels in raw water (ca 100 ppm as nitrate) and high sulfate levels (ca 300 ppm) and ion exchange treatment to reduce nitrate to less than 45 ppm without blending.

5. A significant operating cost for the process is the cost of sodium chloride used as a resin regenerant. A method is presented to estimate the sodium chloride requirements for regenerating the resin used in nitrate removal from waters of various composition. Because anion exchange resins are quite selective for sulfate ion, the presence of sulfate in raw water decreases the efficiency of the resin to absorb nitrate. In this study, however, sulfate was easily removed from the spent resin by the sodium chloride regenerant in nearly stoicheometric proportions whereas excess regenerant is required for nitrate removal. The overall effect of sulfate, however, is to increase the salt required to remove nitrate per unit quantity of water treated. This study also confirmed that large quantities of regenerant (20 pounds per cubic foot of resin) are required to remove most of the nitrate from the spent resin. Not all nitrate need be removed, however, to reduce nitrate levels in treated water to below 45 ppm.

For McFarland wells, the salt cost for lowering nitrate levels to between 30 and 45 ppm ranges between an estimated 1.88 cents for 1,000 gallons of blended water (or $6.13 per acre-foot [A-F]) for Well 2 to 9.96 cents per 1,000 gallons of treated water (or $32.46 per A-F) for Well 3 water. Well 3 represents a particularly difficult water to treat as nitrate levels are

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near 100 ppm and sulfate levels are above 300 ppm. Nitrate levels in Well 2 are near 60 ppm and sulfate levels are near 200 ppm. Salt requirements for waters of other compositions are given (Table 13).

6. To achieve efficient nitrate removal, good brine and influent flow distribution are essential and may require modification in commercially available softening equipment. A method of declassification (thorough mixing) of the resin after downflow regeneration should also be incorporated in the regeneration cycle.

7. Wastewater is produced during the regeneration cycle having an enriched composition of sodium sulfate, chloride, and nitrate. Continuous operation of Well 2 would produce over 12,000 gallons of wastewater per day. Continuous operation of Well 3 would produce an average of 38,686 gallons of wastewater per day.

Theoretical Aspects

1. Previous studies have shown higher resin selectivity for sulfate over nitrate gives rise to some chromatographic enrichment of sulfate in the upper portion of spent columns and enrichment of nitrate in the lower portion. In studies using McFarland Well 3 water, such chromatographic separation was observed only for microporous Type I resins. Microporous Type II and macroporous resins appeared to have nearly equal nitrate and sulfate selectivities. The difference in behavior can be attributed to the greater porosity of microporous Type I resins and/or the lesser steric requirements of the Type I resins. This effect has practical significance because it indicates that nitrate selectivity might be increased over sulfate selectivity by decreasing porosity and modifying the structure about the

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quaternary ammonium ion. To be of practical use, resin selectivity for nitrate must be made to exceed selectivity for sulfate to reverse the order of the enriched portions of the spent resin column.

2. Although some waters can be ion exchanged with minimal salt requirements, the use of sodium chloride as a regenerant has the obvious disadvantage of extensively employing the conventional single bed ion exchange process because of waste disposal requirements. Spent brine can be separated into sulfate rich and nitrate rich fractions for recovery purposes; however, little effort has been spent on recovery processes or on use of alternative regenerants that may make recovery or reuse more practical.

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RECOMMENDATIONS

1. Pilot column studies should be extended and conducted on waters of various composition to verify the method of estimating engineering design parameters and process requirements. These studies should include Type II resins because of their greater capacity and potential for upflow regeneration.

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2. Efforts should be made to reduce regenerant requirements to the lowest level practicable. This can be done by recycling portions of brine and brine rinse as well as backwash waters. Upflow regeneration should also be studied as a method to achieve a low nitrate leakage into the column effluent. This will make all treated water blendable with raw water and could reduce salt requirements per unit quantity of water produced. The use of R.O. in conjunction with ion exchange is another approach. R.O. can reduce the total dissolved solid (TDS) load on the resin and may in some cases provide a brine useful for resin regeneration.

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3. A demonstration plant of 1/2-mgd to 1-mgd capacity should be installed and operated to obtain actual operational experience regarding reliability, health, safety, and costs.

Although the ion exchange process has been used many years in industrial applications and hardness removal from domestic supplies, no significant operating experience has been obtained on a full-scale domestic system for nitrate removal. Use of the process for this purpose cannot be considered as a standard engineering application until the process has been successfully demonstrated on a full scale.

4. Efforts to synthesize nitrate selective resins should continue to make the process more attractive to sulfate laden waters. In such studies, close attention must be paid to the regeneration requirements of the new resins.

SECTION 2

TEST AREA EQUIPMENT AND PROCEDURES

WELL SITE 3, McFARLAND, CALIFORNIA

All tests were conducted at Well Site 3 owned and operated by the McFarland Mutual Water Co. (McMWCo). Site improvements were designed for Well 3 to accommodate equipment for conducting both the field tests and laboratory scale experiments. Water was supplied directly to a concrete pad and trailer from an existing surge tank. All product and wastewaters were discharged from the pad directly into the city sewer system. The 30-foot by 32-foot pad was large enough to accommodate a field-test ion exchange system, a field-test R.O. system, and a single module R.O. system with the necessary tanks for temporary water storage. A trailer adjacent to the pad housed a field office and limited laboratory facilities. An industrial steel roof was installed over the entire concrete pad.

LABORATORY ION EXCHANGE COLUMNS

Laboratory ion exchange columns were fabricated from 4-foot lengths of 2-inch inside diameter (ID) acrylic resin pipes and polyvinyl chloride (PVC) FLO-CONTROL adapters used as end fittings. A Masterflex Model 7017 was capable of delivering up to 1,350 milliliters (ml) per minute through a 24-inch bed of resin in the 2-inch-ID columns (1 bed volume = 1,245 ml). A source of Well 3 water was available in the trailer. Synthetic mixtures were

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prepared and pumped directly at measured flow rates with the Masterflex pump through the ion exchange columns.

PILOT ION EXCHANGE SYSTEM - DESCRIPTION

A Culligan HI-FLO 5 Water Softener Model 150 was installed on the pad at Well 3. A sketch of the system is shown in Figure 2. The completely automatic water softener was converted to a semiautomatic anion exchanger by installing an industrial timer and anion exchange resin (Duolite A-101D). Six hydraulic valves controlled by a motor-driven pilot valve determine various cycles of operation including service, backwash, brine rinse, and fast rinse. An industrial timer was installed for selection of duration for the latter three cycles. The service cycle duration can be controlled by a clock mechanism allowing regeneration as frequently as 12 hours or can be manually set to allow shorter service cycles.

The system was connected directly to the Well 3 water supply by 1-inch PVC pipe. Replumbing to 2-inch pipe was later found necessary to gain maximum flow rates of 6 cubic feet per minute (cfm) during the service period.

A flowmeter was connected to the outlet pipes which discharged directly to a drain. Inlet and outlet control valves were also installed.

Duolite A-101D (4.36 cubic feet), a Type I resin, was placed in the 20-inch-diameter resin tank. This was sufficient resin to provide 24 inches of bed depth. It was found that during the 10-gpm backwash, some resin was thrown into the drain line. Backwash rate could be decreased but not without affecting the brine draw mechanism. A 50-mesh stainless-steel screen was installed in the feed inlet at the top of the tank (through which the backwash

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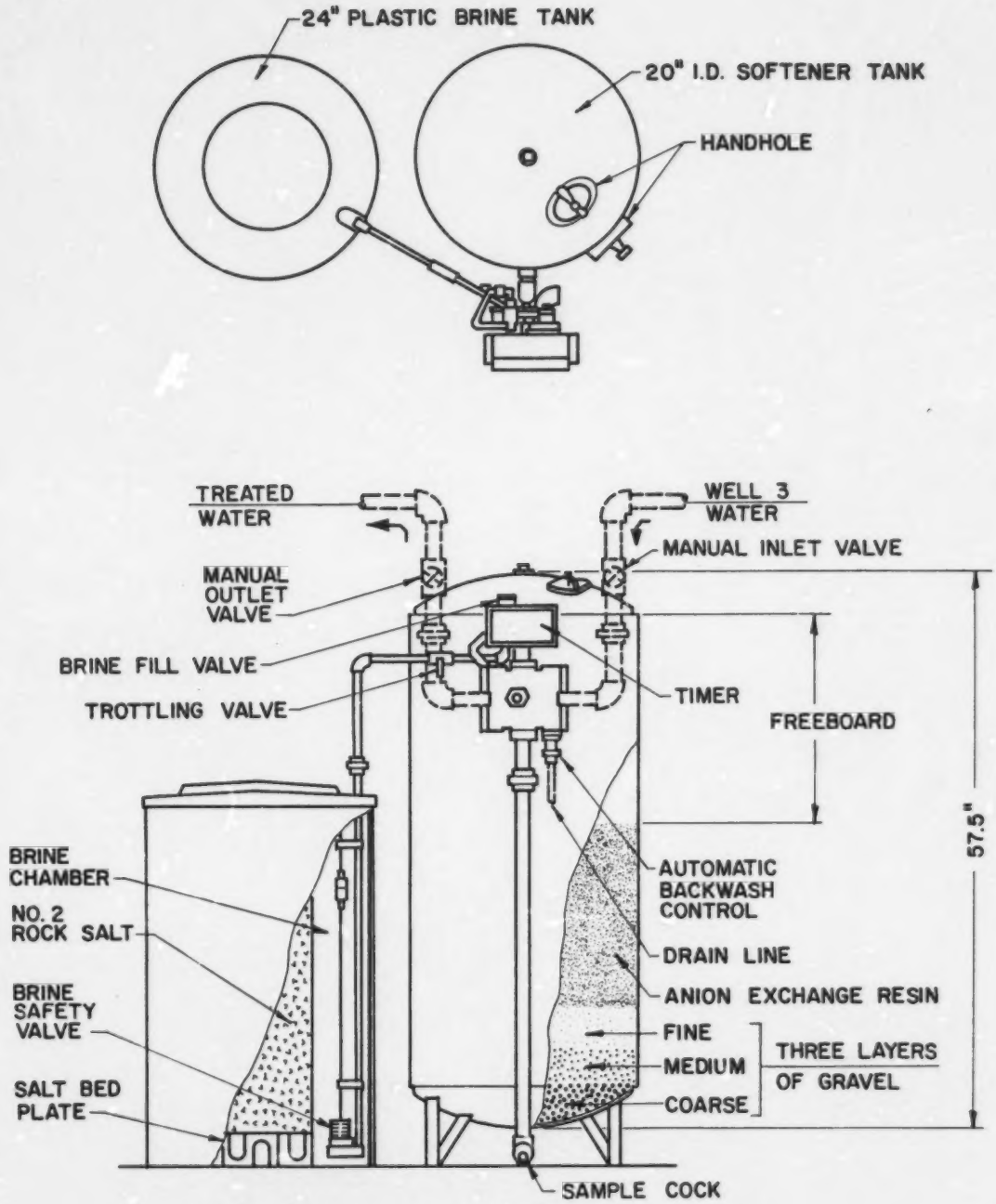

FIGURE 2. HI-FLO 5 WATER SOFTENER SYSTEM

water exits) to prevent resin loss and backwash rate was left at 10 gpm. Salt was charged to the brine tank manually, and water was automatically fed to the tank at a predetermined flow rate during the service cycle. An adjustable timer controlled the time of charging water to the tank (up to 60 minutes). During regeneration, all saturated brine was drawn from the brine tank by an eductor. The brine mixed with water in an approximate ratio of one part brine to two parts water and downflowed over the resin. Thus the amount of salt used for regeneration was indirectly determined by the amount of water flowing into the brine tank during the service cycle. The manufacturer provides a table relating time of filling the brine tank to amount of salt used in regeneration. This was not the most efficient system for research purposes where it is desirable to know more exact amounts of salt used. Consequently, the brine draw system was later altered (see page 39).

ANALYTICAL PROCEDURES

Nitrate Analyses

The ion exchange column tests and operation of the HI-FLO 5 System required rapid and frequent nitrate analyses. The HACH NI-12 test kit (range 0 to 50 milligrams per liter [mg/l] N) and HACH N-14 (range 0 to 1 mg/l N) were used for this purpose. The test kits, however, were not used without calibration or comparison with results obtained from state of California certified laboratories. Analyses were also performed on unknown nitrate samples supplied by the Environmental Protection Agency (EPA) laboratory in Cincinnati. HACH kit results without calibration consistently gave high nitrate results. This was determined by use of the

standard additions method using certified nitrate standards and comparison with results obtained from a certified laboratory. The standard additions method was far too time consuming to be used for each nitrate analysis required. Consequently, the HACH kits were calibrated as described below.

HACH kits are supplied with numerically marked color wheels. The numbers correspond to mg/l N and are read below a pointer in the window over the color wheel. Because the pointer and graduated scale are about 5 millimeters apart, accurate readings were not possible. A hairline was glued to the window of the test kits to aid in reading the scale to 0.1 division. Several solutions were then prepared of varying nitrate concentrations from certified nitrate standards. Each solution was read on the corresponding HACH test kit with the hairline indicator and a calibration curve for each test kit was developed. Figures 3 and 4 show the accuracies of the two kits.

The NI-12 is linear in the range 0 to 12 mg/l N but consistently over 2 mg/l N too high. Considerable curvature then develops at about 15 mg/l N. The precision obtained in the region of 10 mg/l N is $10.0 \pm .4$. A standard "practice" solution supplied by EPA with a concentration of 10.2 mg/l N was read as $10.2 \pm .4$ using the NI-12 kit and Figure 3 as a calibration curve.

The N-14 kit gave much closer readings to the standard values as seen in Figure 4. A standard "practice" solution supplied by EPA with a concentration of 0.22 mg/l N was read as 0.22 ± 0.004 directly from the N-14 readout dial.

EPA-supplied unknowns were determined as 0.710 and 6.00 mg/l N and compared by EPA to actual values of 0.700 and 6.00 mg/l N, respectively.

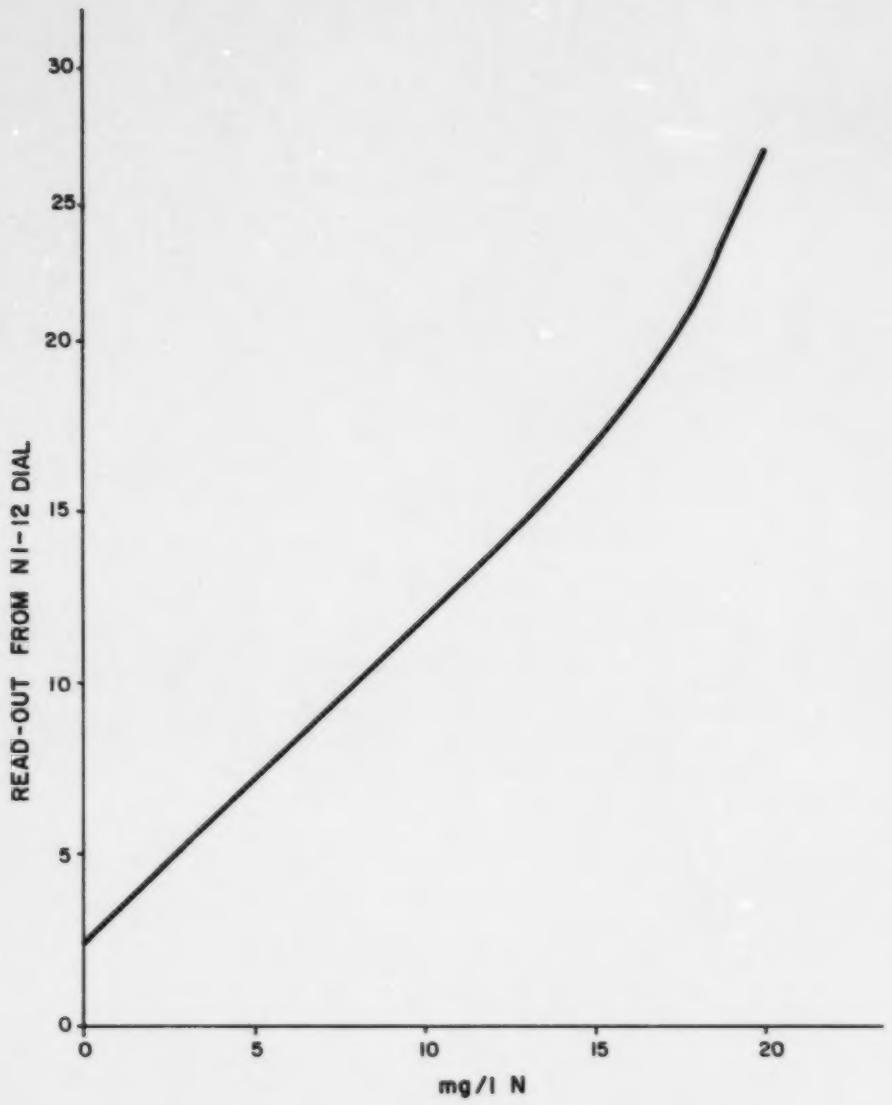

FIGURE 3. CALIBRATION CURVE FOR HACH NI-12

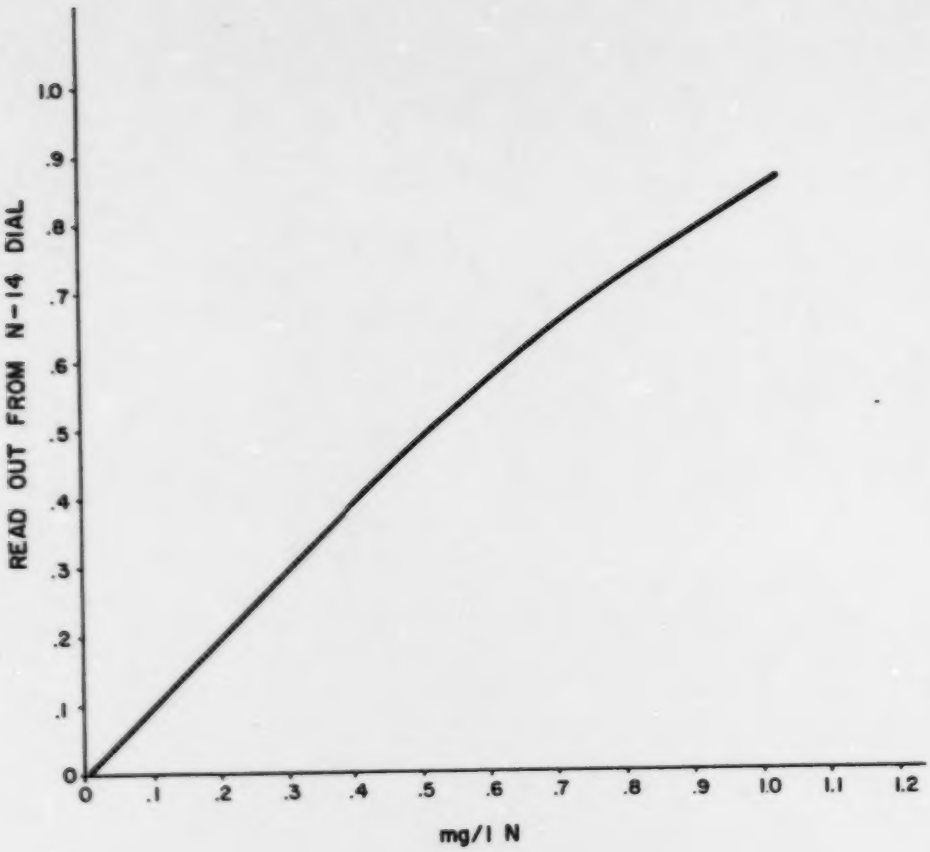

FIGURE 4. CALIBRATION CURVE FOR HACH N-14

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A quality control program was initiated in January, 1980, to compare field nitrate tests with those obtained by a certified laboratory (Table 1).

TABLE 1. NITRATE ANALYSES (ppm)

Date	HACH Test Kit Results	Certified Laboratory
1-15-80	20.2	20.8
1-15-80	112.6	93.0
2-01-80	29.9	31.9
2-18-80	85.0	88.6 and 92.1 (same sample)

Sulfate Analyses

Sulfate analyses were performed by the turbidimetric method (American Public Health Association [APHA] Standard Methods, 14th edition, 496, 1975) using HACH reagents and a HACH DR/2 spectrophotometer.

Chloride Analyses

Chloride analyses were performed by Mohr argentometric method (APHA Standard Methods, 14th edition, 303, 1975).

Bicarbonate Analyses

Bicarbonate analyses were performed by the alkalinity titration method (APHA Standard Methods, 14th edition, 278, 1975).

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SECTION 3

ION EXCHANGE COLUMN TESTS

INTRODUCTION TO COLUMN TESTS

Column tests with five different resins were made at the beginning of the effort. Column tests are recommended by resin manufacturers to establish important processing parameters and information, such as length of service period, ion breakthrough curves, flow rates for service, and regeneration (Reference 1). The performance of columns provides baseline data by which performance of large-scale equipment can be measured because of the nearly ideal hydraulic conditions and degree of control which can be achieved in columns. Additional advantages of column testing on this program are ability to use sample quantities of resins (about 1 kilogram) to screen resins and capability to use feed waters of various composition.

RESINS TESTED

Five ion exchange resins were selected for study with the 2-inch laboratory size ion exchange columns. The selection was based on previous work (Reference 2) which tested 32 commercially available anion exchange resins for application of both single-bed and two-bed processes. Because only the single-bed process was chosen for this study, tests were limited to strong base anion exchange resins. The above study and discussions with resin manufacturers indicated that none of the resins would exhibit exceptional selectivity for nitrate ion over other major anions. Some differences among

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resins could, however, be expected, such as differences in ion exchange capacity, release of amine odors or taste, useful lifetime, and ease of regeneration. This study was thus restricted to strong base anion resins differing in resin type (Type I or Type II) and porosity type. The resins listed in Table 2 were the subjects of the column studies described below.

TABLE 2. STRONG BASE ANION EXCHANGE RESINS

Manufacturer's Designation	Quaternary Amino Type	Porosity Type	Advertised Capacity (meq/ml)
Duolite A-101D	I	Semiporous	1.30
Duolite A-104	II	Micro	1.50
Dowex SAR	II	Micro	1.40
Amberlite IRA-900	I	Macro	1.00
Amberlite IRA-910	II	Macro	1.00

COLUMN TESTS

Procedures

Conditioning of Resins - Resins were conditioned according to manufacturers' recommendations for anion exchangers. A 2-inch-diameter column was filled with a resin water slurry to give a resin bed depth over 24 inches and treated as follows:

1. Flow 2 BV of 1.5 N NaOH through resin (20 minutes); 125 ml/minute.

2. Wash out caustic with 5 BV of soft or deionized water (30 minutes); drain water from resin, leaving 1 inch above top of bed.

3. Flow 2 BV of 2 N HCl through the resin (20 minutes).

4. Wash out the acid with 5 bed volumes of water (30 minutes); drain water from resin to within 1 inch of top of bed.

5. Repeat the caustic rinse-acid rinse cycle outlined in Steps 1 to 4.

The resin was in the chloride form and was removed from the column, air dryed, then weighed and stored for further use.

Column Operation - Laboratory ion exchange columns were operated according to procedures outlined in manuals supplied by resin manufacturers (Reference 1). The following representative conditions were chosen for the experimental column work:

Column Size	2-inch-ID by 4-foot length
Bed Depth	24 inches
Cross-Sectional Area of Column	3.14 in^2; 20.26 cm^2; 0.022 ft^2
Bed Volume of Ion Exchange Resin	1,245 ml; 0.044 ft^3
Exhaustion Rate	0.33 to 1.5 BV/min 415 to 1,868 ml/min 0.110 to 0.493 gal/min 5 to 22 gal/ft^2/min 2.5 to 11.2 gal/ft^3 resin
Regenerant Composition	6 percent sodium chloride 60g NaCl/l 1.02 eq NaCl/l
Regenerant Rate	4 BV/hr 4,980 ml/hr 1.315 gal/hr 59 gal/hr/ft^2
Regenerant Contact Time	90 min
Regenerant Direction	Downflow

Backwash Rate	Sufficient to achieve 30 to 100 percent bed expansion
	5 to 10 min
Rinse Time	30 to 45 min
Rinse Rate	0.33 BV/min 5 gal/ft^2/min

Tests on Well 3 Water

Ion exchange experiments were conducted with the five strong base anion exchange resins listed above in the 2-inch-diameter columns. Flow rates were held near 1/3 BV per minute for most runs. Water directly from Well 3 was used either diluted with deionized water or undiluted.

An automatic sampler was constructed to obtain effluent samples at least once every 60 minutes. A flowmetering device was also constructed to record the flow rate through the column. This was necessary because it was observed that flow rate changes varied slightly over long periods of operation and required either frequent readjustment or automatic recording.

The resins, feed water compositions, and bed volumes treated to breakthrough for nitrate and sulfate ions are given in Table 3. Typical breakthrough curves are given in Figures 5 through 12.

Tests With Synthetic Mixtures

Synthetic water compositions containing the major anions nitrate, sulfate, bicarbonate, and chloride were prepared for the ion exchange column experiments. Mixtures were prepared using Well 3 water mixed with either deionized water or product of an R.O. system operating on Well 3 water. In some cases, sulfate or nitrate concentrations were adjusted by addition of sodium nitrate or sodium sulfate. The synthetic solutions are listed in

TABLE 3. ION EXCHANGE COLUMN EXPERIMENTS WELL 3 AND SYNTHETIC MIXTURES

Run No.	Resin		Exh. Rate (BV/m)	Feedwater Composition (meq/l)				Bed Volumes to Breakthrough		Figure No.
	I.D.	Type		NO_3^-	HCO_3^-	Cl^-	$SO_4^=$	$SO_4^=$	NO_3^-	
11078	A-101D	I	.33	1.56	1.63	2.51	5.93	ND[a]	157	None
02199	A104	II	.33	1.11	2.39	2.01	4.68	242	240	6
02219	A-101D	I	.33	1.17	2.39	2.01	4.68	232	198	5
03059	A104	II	.33	1.91	2.89	2.82	6.70	165	172	7
03299	Dowex SAR	II	.33	1.73	2.73	2.67	7.65	183	184	8
06229	IRA-900	I	.33	1.79	2.49	2.82	7.18	138	140	9
06279	IRA-910	II	.33	1.79	2.49	2.82	7.18	133	122	10
02290	A-101D	I	.36	1.17	1.74	2.67	7.32	163	147	11
02260	A-101D	I	1.10	1.26	1.61	2.72	7.74	174	159	11
02230	A-101D	I	1.56	1.48	1.39	2.56	6.87	188	176	11
03069[b]	A-101D	I	.33	0.85	1.50	1.45	3.35	ND	300	12
03050[b]	A-101D	I	.33	1.63	1.14	1.41	3.64	318	248	19
03140[b]	A-101D	I	1.0	1.12	1.08	2.33	8.33	168	163	20

[a] Not determined.
[b] Synthetic blends.

Table 3 along with bed volumes to nitrate and sulfate breakthrough. Breakthrough curves are given in figures listed in Table 3. Interpretation of these curves is given in Section 4, THEORETICAL CONSIDERATIONS AND DATA INTERPRETATION.

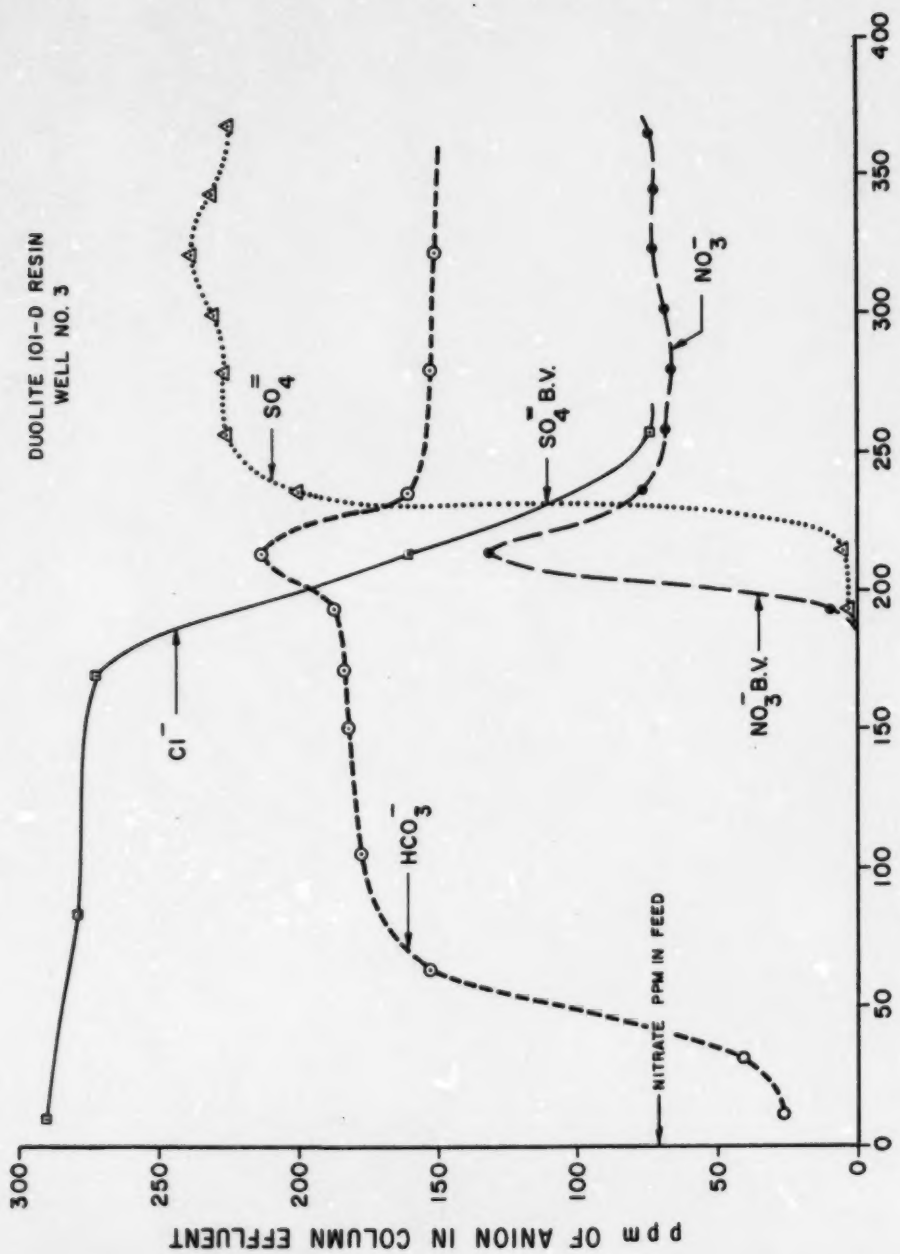


FIGURE 5. ION EXCHANGE COLUMN EXPERIMENT 02219

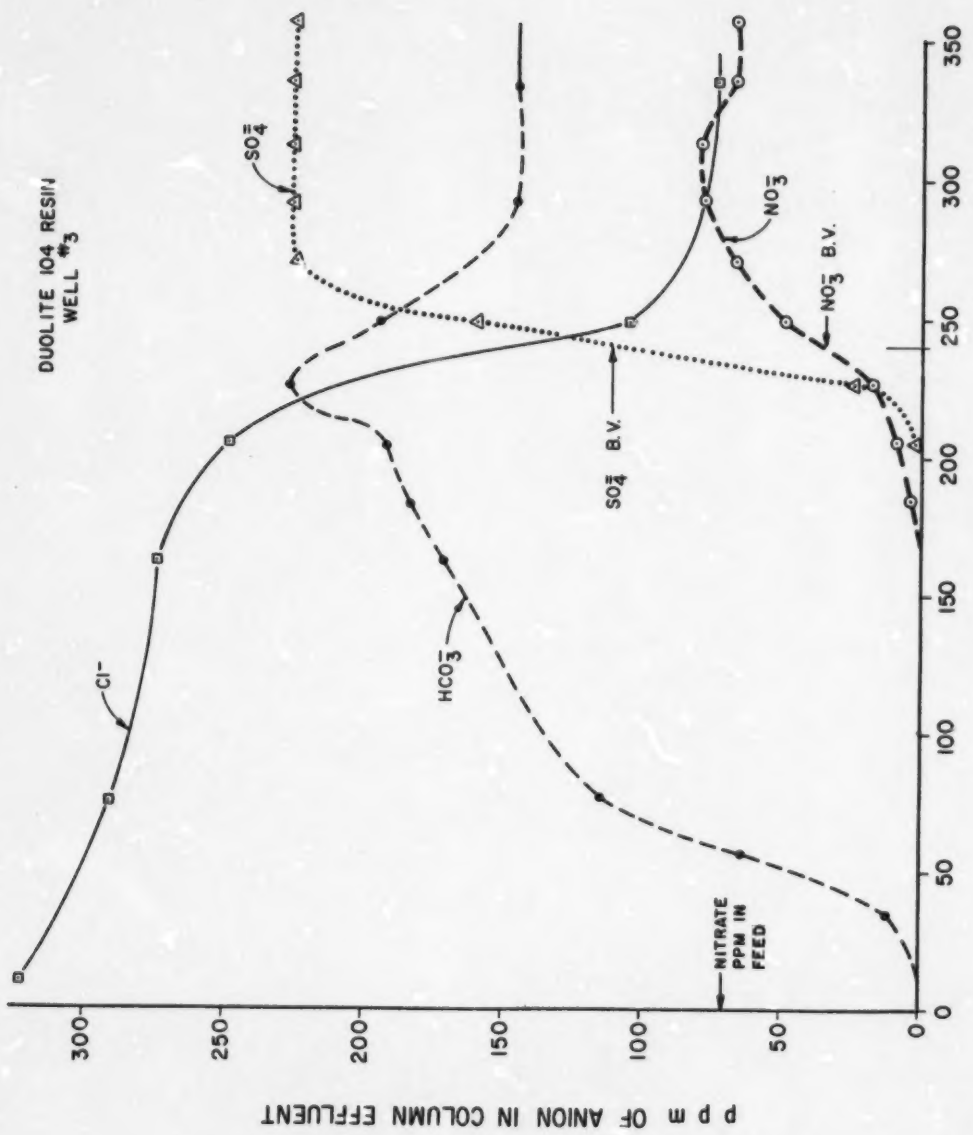


FIGURE 6. ION EXCHANGE COLUMN EXPERIMENT 02199

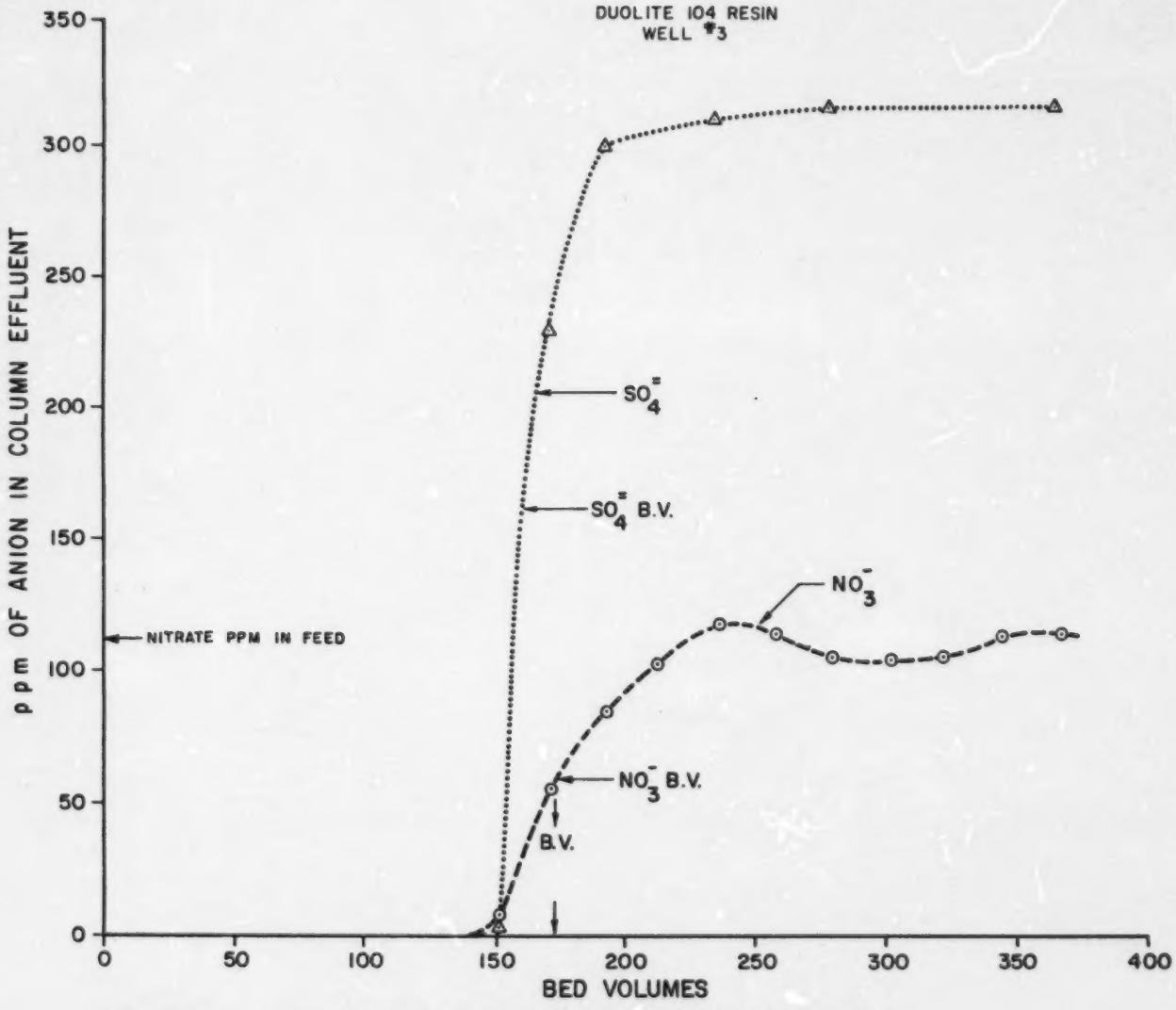


FIGURE 7. ION EXCHANGE COLUMN EXPERIMENT 03059

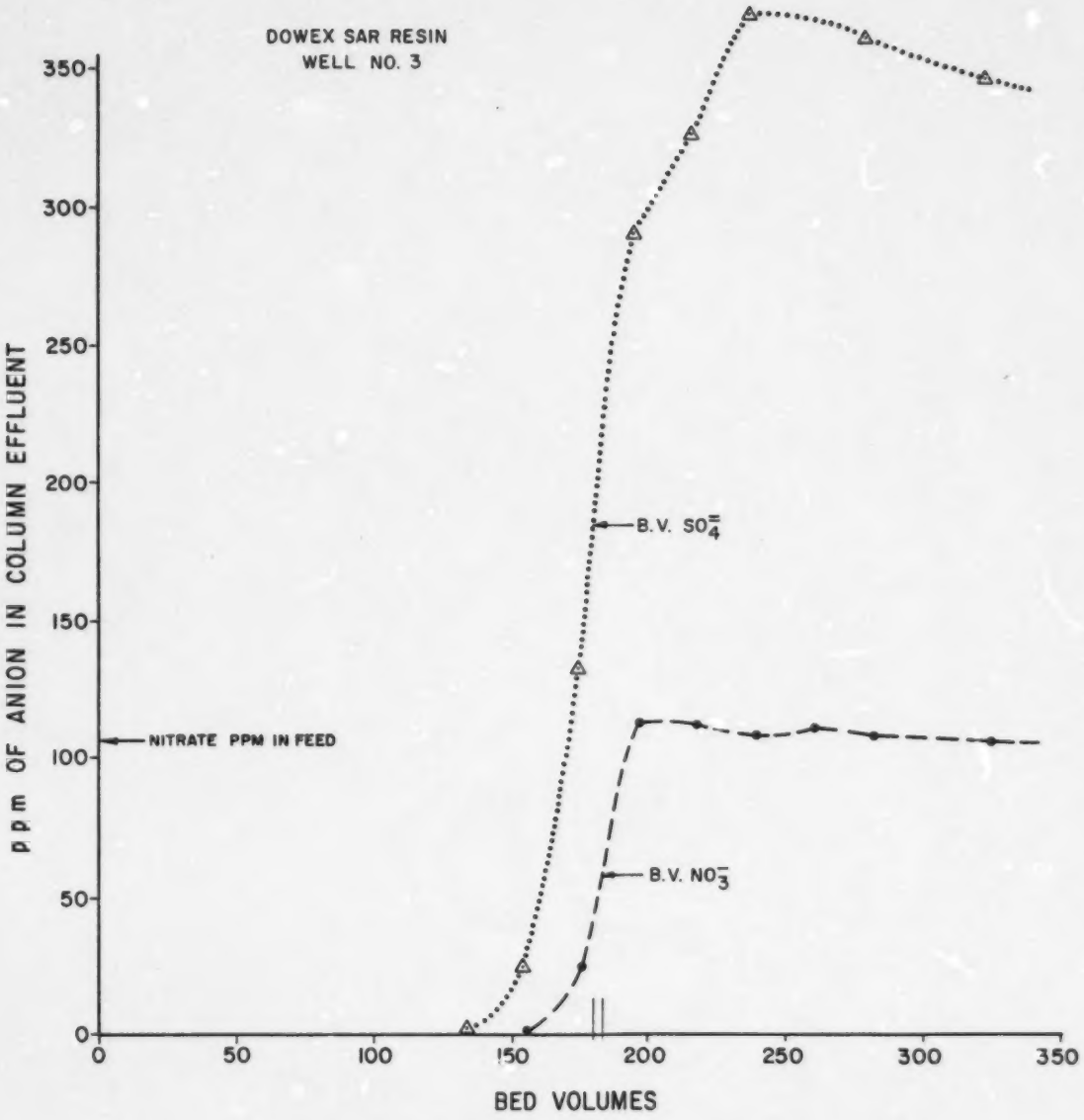


FIGURE 8. ION EXCHANGE COLUMN EXPERIMENT 03299

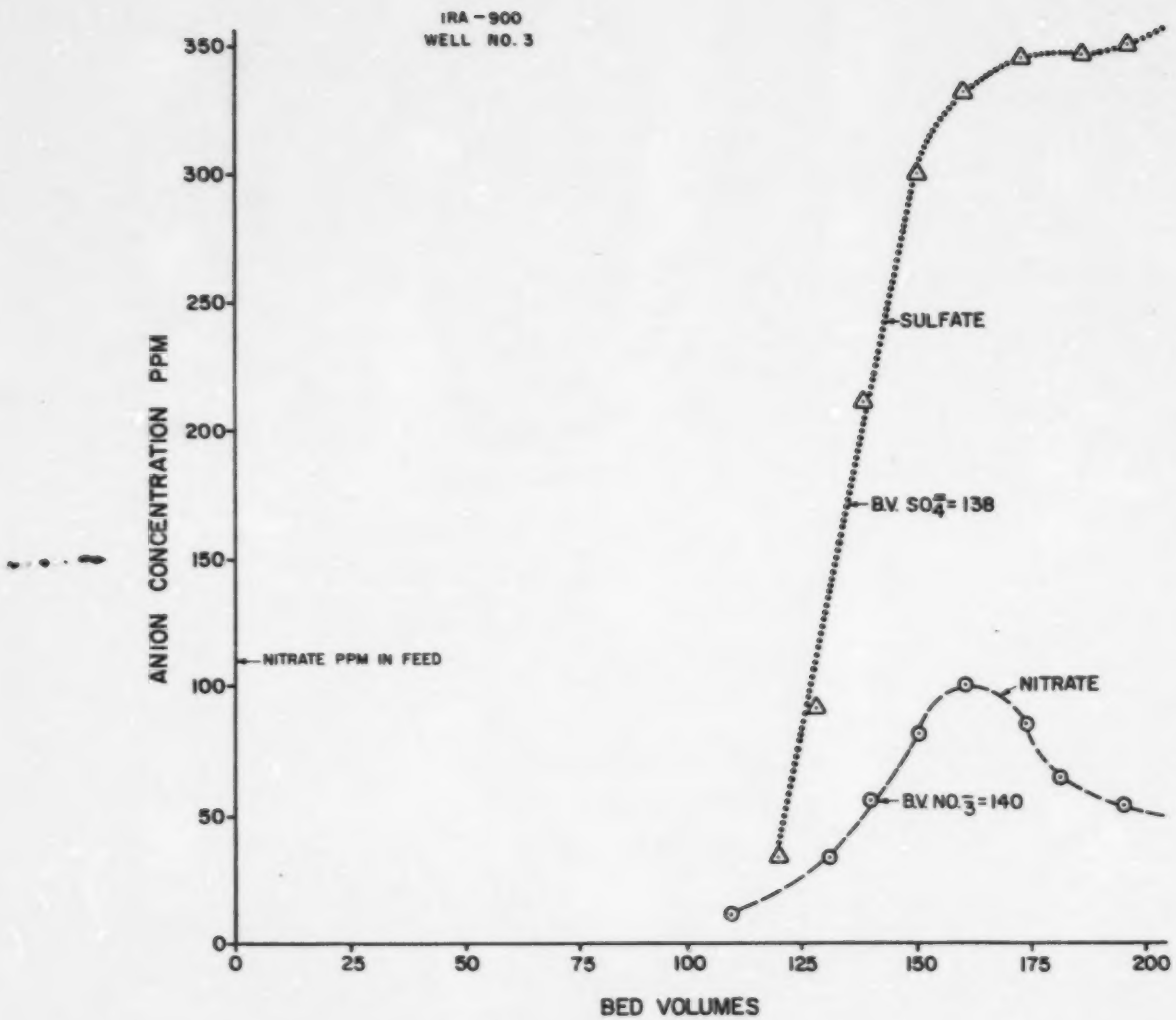


FIGURE 9. ION EXCHANGE COLUMN EXPERIMENT 06229

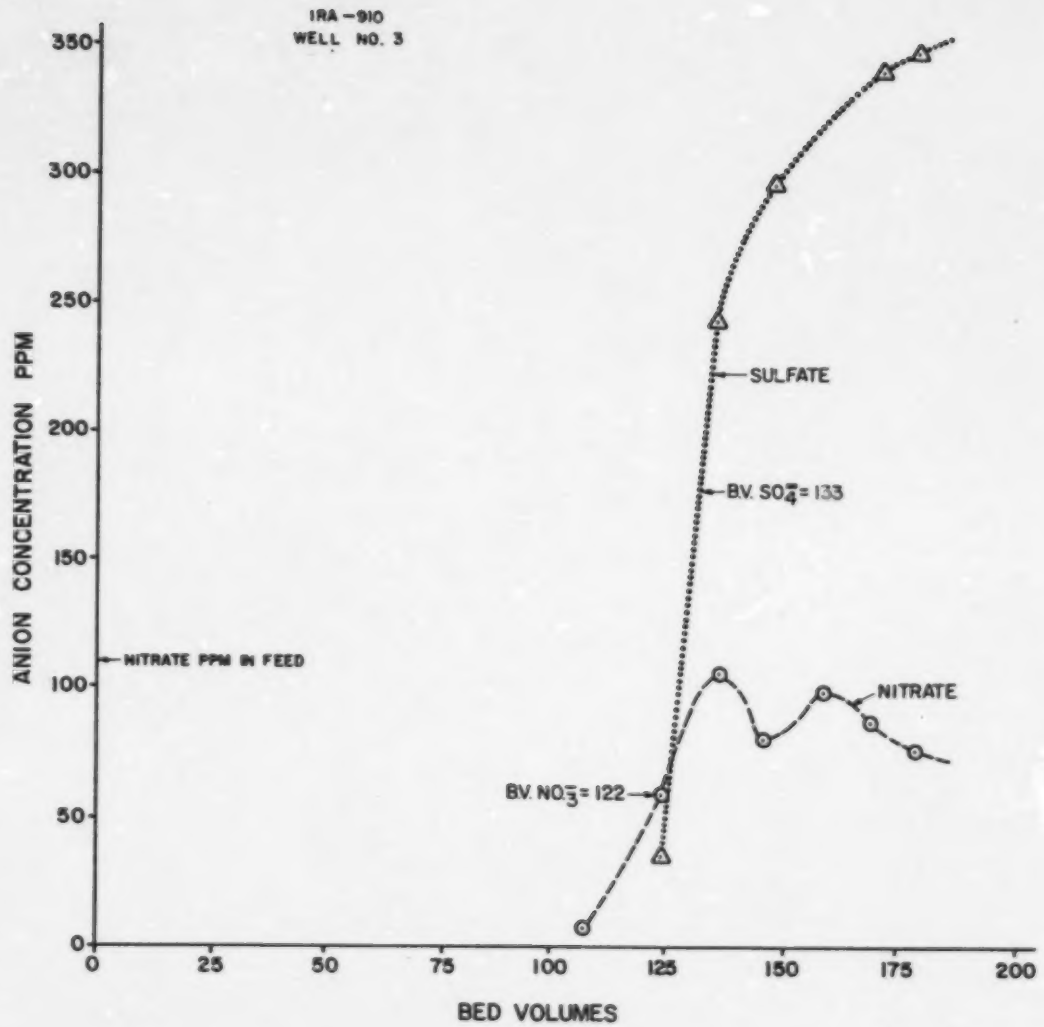


FIGURE 10. ION EXCHANGE COLUMN EXPERIMENT 06279

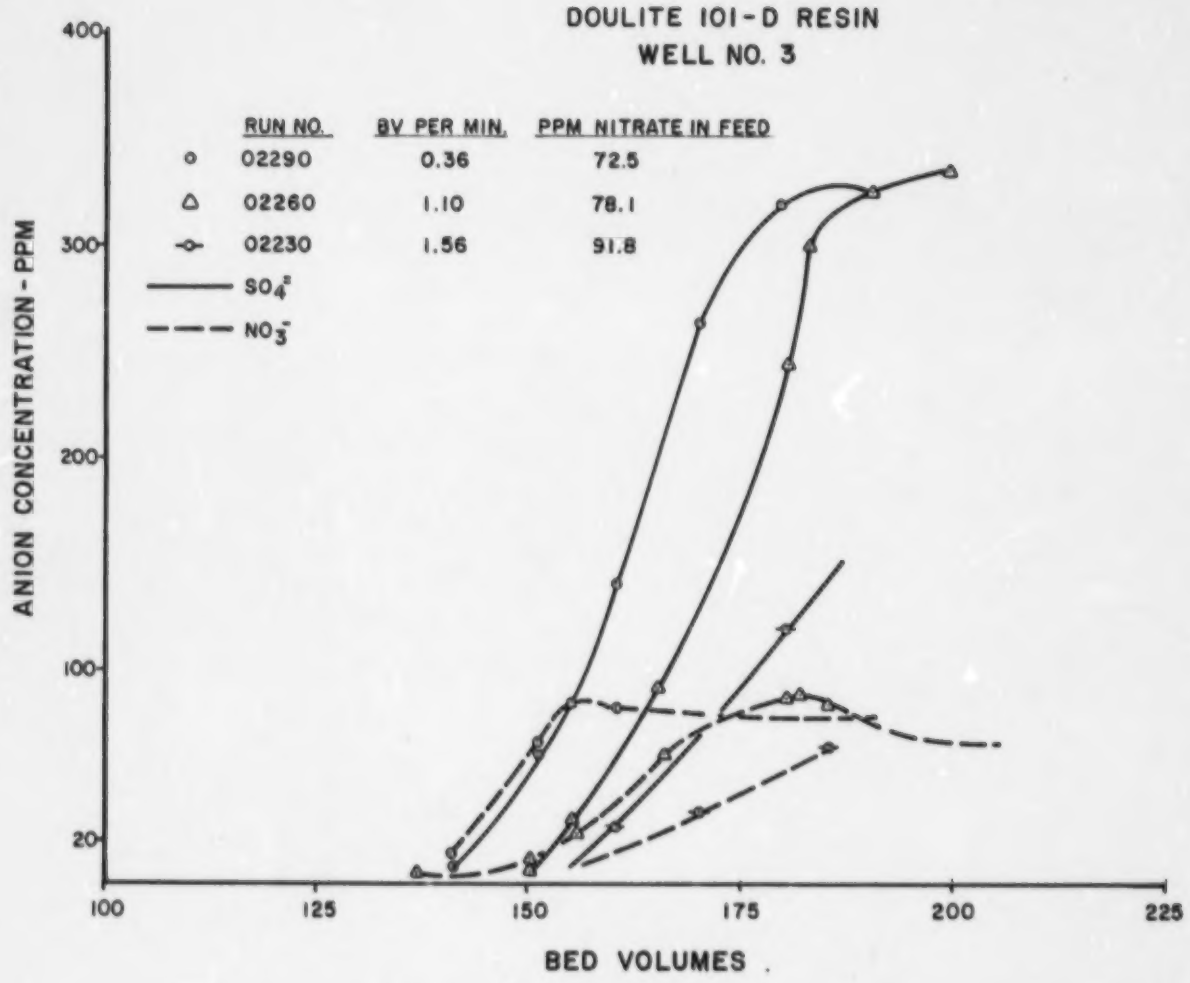


FIGURE 11. ION EXCHANGE COLUMN EXPERIMENTS - FLOW RATE EFFECT

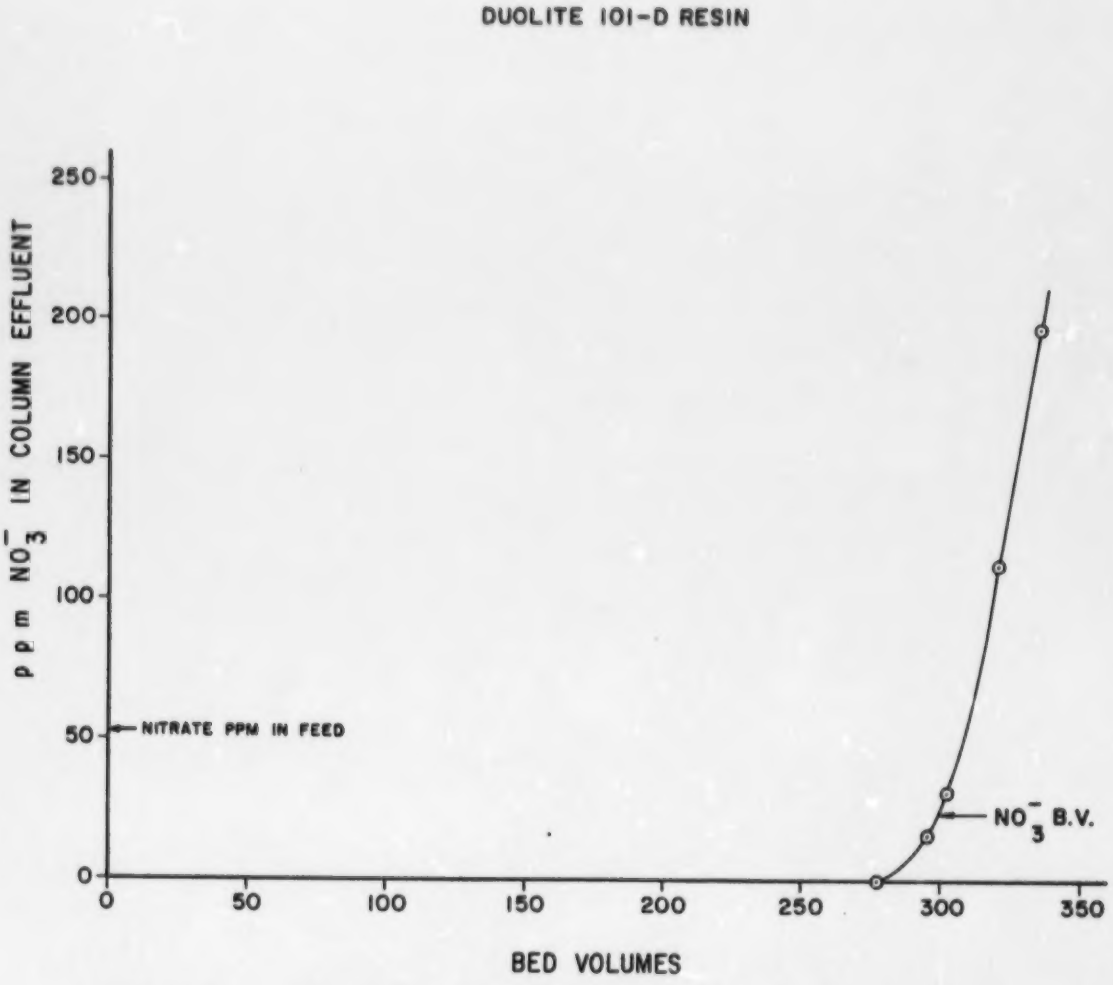


FIGURE 12. ION EXCHANGE COLUMN EXPERIMENT 03069

Column Regeneration Experiments

In the above-described column tests, the exhausted resins were regenerated with 6 BV of 6 percent sodium chloride. Typical regeneration curves are shown in Figure 13 for the Duolite resins. For the A-104 resin, 325 milliequivalents (meq) of nitrate were recovered compared to 323 meq absorbed by the resin. For the A-101D resin, 282 meq of nitrate were recovered compared to 288 meq absorbed.

Experiments were also conducted in regeneration of columns fully loaded with nitrate ion with sodium chloride regenerants and a brine obtained from an R.O. system operating on Well 3.

In a typical experiment, a laboratory column filled with Duolite A-101D resin was treated with a 1 N solution of sodium nitrate. Three BV of the nitrate solution were slowly passed through to ensure saturation with nitrate. The column was then treated with 6 BV of 6 percent sodium chloride. Each BV through the column was analyzed for nitrate. The column was again saturated with nitrate as above, then treated with 60 BV of an R.O. concentrate at 20 BV per hour. The composition of the major anions in the R.O. concentrate was:

Nitrate	115.2 ppm
Sulfate	725
Chloride	154
Biocarbonate	159

Regeneration with 6 BV of sodium chloride was repeated as above and each BV of regenerant was analyzed for nitrate and sulfate.

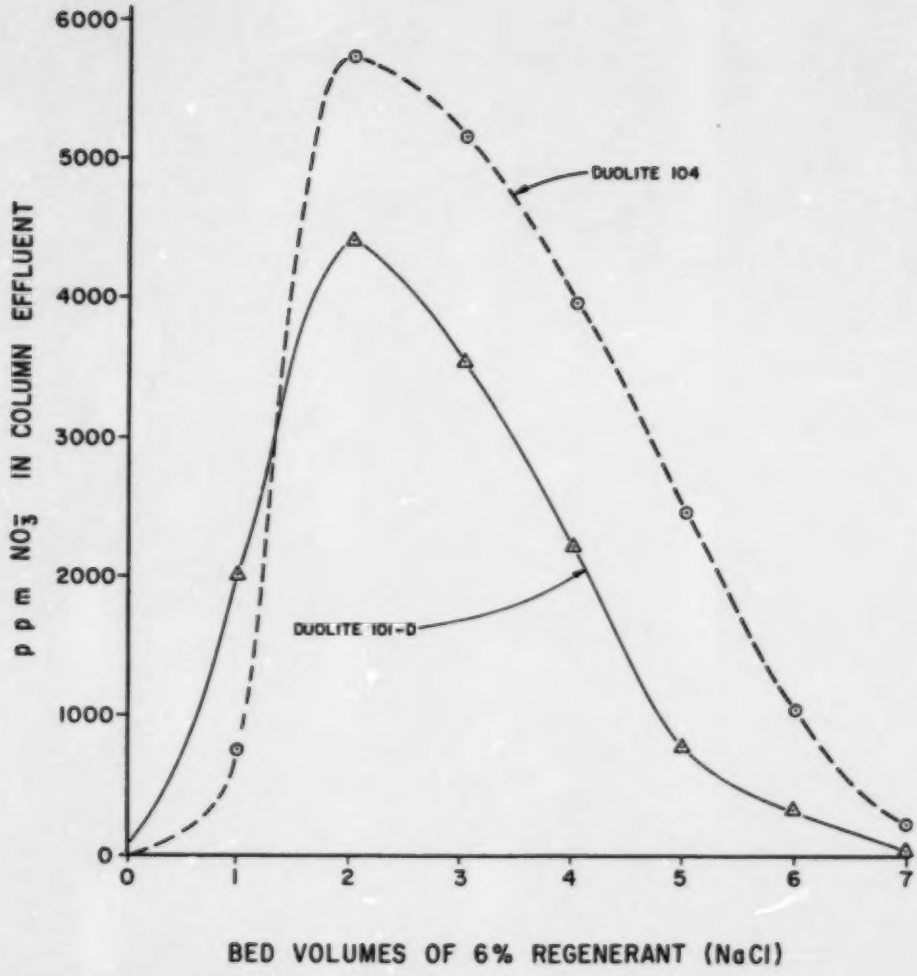


FIGURE 13. ION EXCHANGE COLUMN REGENERATIONS 03069 AND 03079

The results are shown in Figure 14. The data were converted to chemical equivalents and plotted as Curves A and B to indicate the equivalent fraction of the column which contained nitrate after the passage of each BV of regenerant.

Curve B in Figure 14 shows that pretreatment with the R.O. concentrate removes nearly 90 percent of the nitrate from the column. Subsequent treatment with 1 BV of regenerant does little to remove nitrate since it is removing sulfate at this point. An additional 0.5 BV of regenerant brings nitrate down to a level where 3.0 BV of regenerant are required for the unpretreated columns (Curve A). Columns regenerated to this level would give a nitrate leakage of 5.6-ppm nitrate.

Other data on regeneration was obtained with the HI-FLO 5 ion exchanger described in Section 4 of this report.

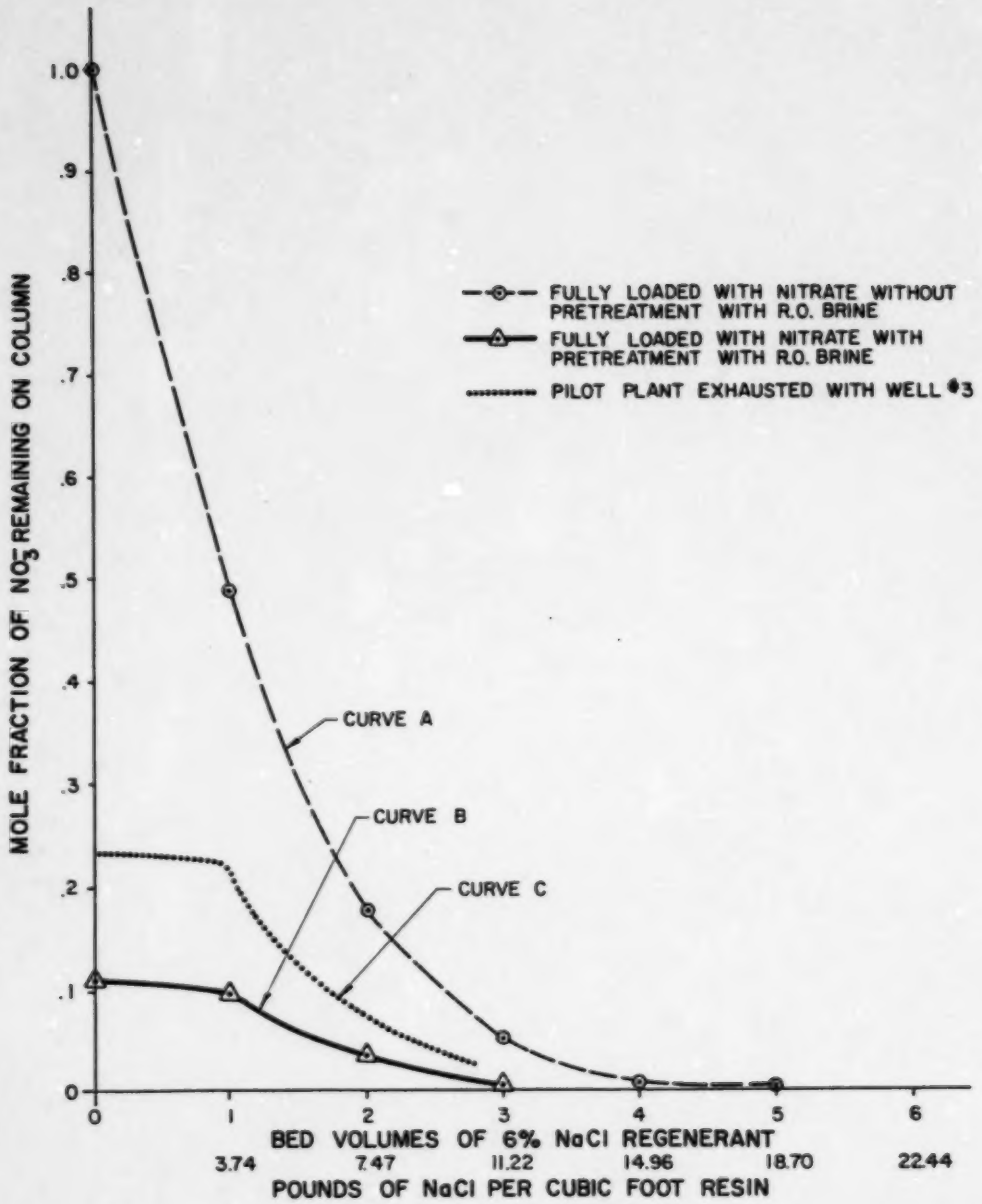


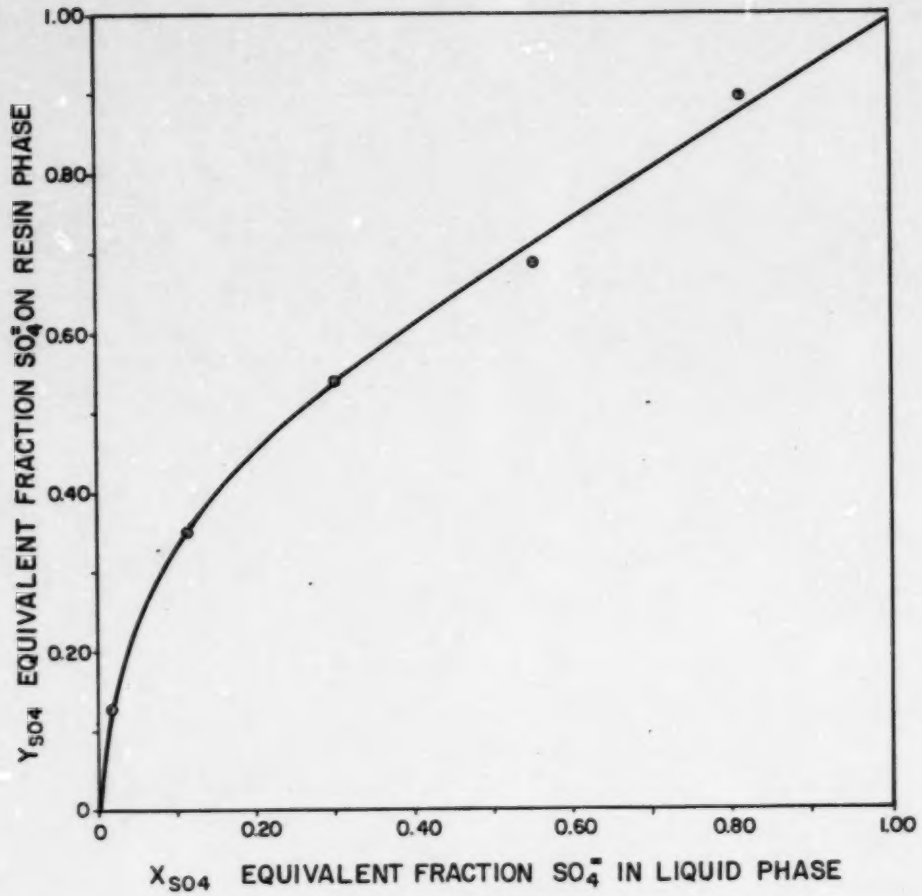
FIGURE 14. COMPARISON OF NITRATE REMAINING ON COLUMNS DURING REGENERATION

SECTION 4

THEORETICAL CONSIDERATIONS AND DATA INTERPRETATION

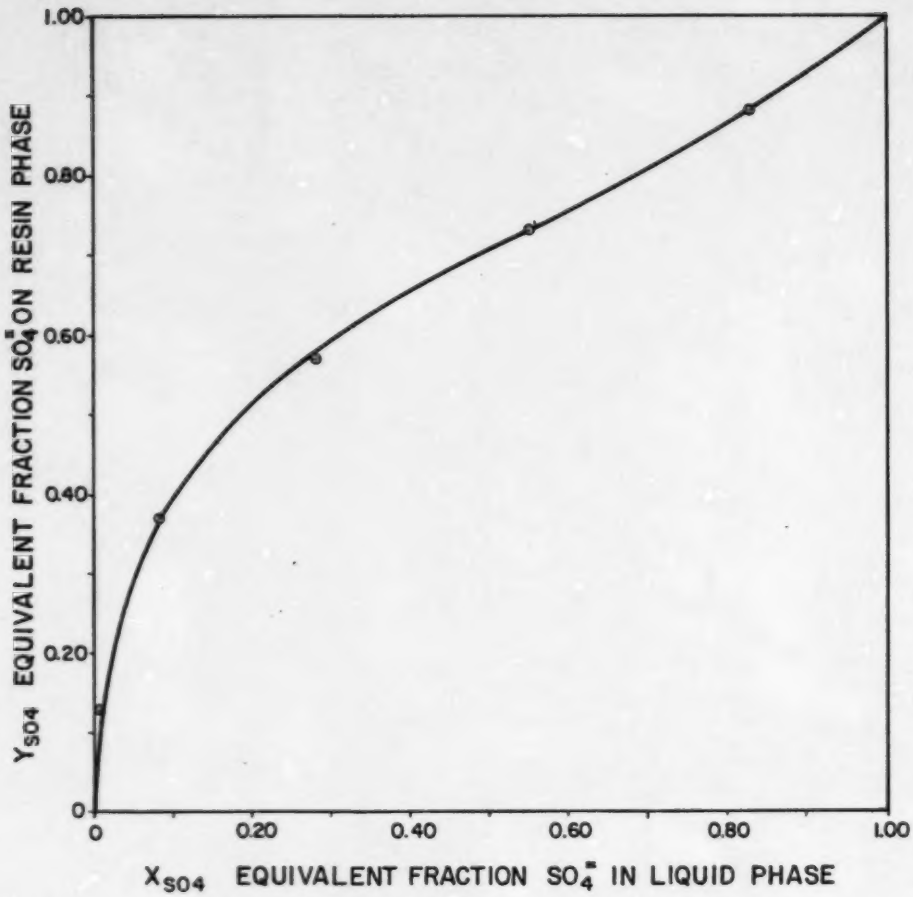
PREVIOUS WORK

The experimental work done on this program is subsequent to work done by Clifford and Weber (Reference 2). In that effort, 32 commercially available anion resins were studied in both equilibria and laboratory column experiments. Binary isotherms were obtained under equilibrium conditions and separation factors were related to resin properties. Examples of binary isotherms are reproduced here in Figures 15, 16, and 17 for the two Duolite and one Amberlite resins studied in that effort which also included chromatographic column studies at 2.5 to 5 BV per minute exhaustion rates. At these flow rates, equilibrium was achieved on the column whose performance could then be related to the isotherm data. The work of Clifford and Weber is also referred to here as an excellent general review of ion exchange materials and their use for nitrate removal. The primary thrust of the work was to study ion exchangers for the purpose of comparing a single-bed process to a two-bed process. Important parameters, such as flow rate and resin regeneration aspects of either process, were thus not studied for optimum performance. The work was also limited to water of a single composition and thus not directly applicable to well water found in McFarland, California. Frequent reference to the Clifford and Weber work will be made throughout this discussion. Important conclusions drawn by Clifford and



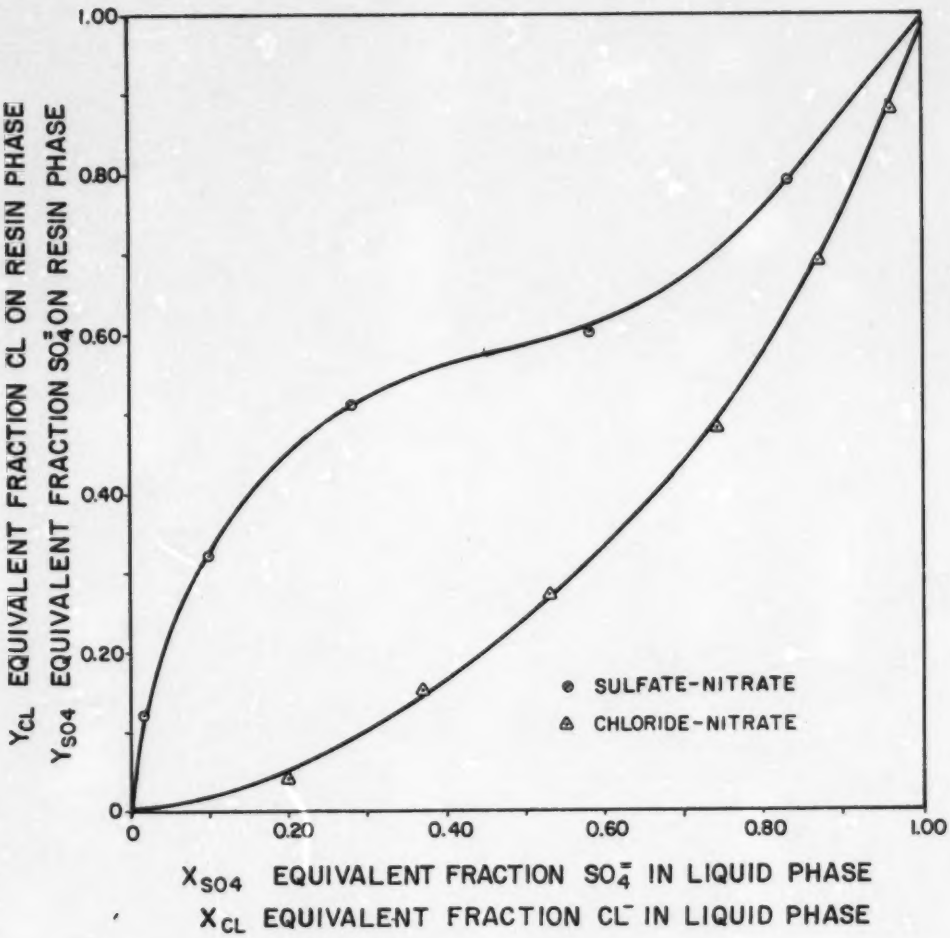
RESIN NUMBER 24
DUOLITE A 101 D, "IMPROVED" POROSITY GEL
STYRENE-DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.3 MEQ/ML

FIGURE 15. 25°C. BINARY ION-EXCHANGE ISOTHERM



RESIN NUMBER 25
DUOLITE A-104, MICROPOROUS GEL
STYRENE-DVB MATRIX
TYPE I & II QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.5 MEQ/ML

FIGURE 16. 25°C. BINARY ION-EXCHANGE ISOTHERM



RESIN NUMBER 17
AMBERLITE IRA 900, MACROPOROUS RESIN
STYRENE - DVB MATRIX
TYPE I, QUATERNARY-AMINE FUNCTIONALITY
TOTAL CAPACITY = 1.0 MEQ/ML

FIGURE 17. 25°C. BINARY ION - EXCHANGE ISOTHERM

Weber, which are pertinent to this work, are those relating to the selectivity that all anion exchange resins tested show for sulfate over nitrate ion and the resin properties influencing that selectivity.

RESIN-ION EQUILIBRIA

Selectivity Coefficients

Selectivity coefficients can be used to relate column composition to solution composition. These coefficients are used by Anderson (Reference 3) to relate column composition to solution composition.

In the case of two monovalent ions in solution which compete for an ion exchange site on a given resin, the following chemical equilibrium can be written in the case of nitrate and chloride ion competition

$$NO_3^- + \overline{Cl} \rightleftharpoons \overline{NO_3} + Cl^-$$

$$K_{Cl}^{N} = \frac{[\overline{NO_3}]\ [Cl^-]}{[\overline{Cl}]\ \ [NO_3^-]} \qquad \text{Equation (1)}$$

where bracketed terms are concentrations of the ions expressed as equivalents per liter in solution or on the ion exchange resin (barred terms). If Equation (1) is written in terms of equivalent fraction concentration terms, Equation (2) is obtained (see Reference 3):

$$\frac{\overline{X_N}}{1 - \overline{X_N}} = K_{Cl}^{N} \times \frac{X_N}{1 - X_N} \qquad \text{Equation (2)}$$

where $\overline{X_N}$ = equivalent fraction of nitrate on resin

X_N = equivalent fraction of nitrate in solution

The total concentration of ions in solution and on the resin does not appear in Equation (2).

In the case of a monovalent ion and divalent ion in solution competing for resin ion exchange sites, such as nitrate and sulfate ion competing for sites on an ion exchange resin, the following chemical equilibrium and equilibrium constants can be written:

$$SO_4^{=} + \overline{2NO_3} \rightleftharpoons 2NO_3^{-} + \overline{SO_4}$$

$$K^S = \frac{[NO_3^-]^2 \ [\overline{SO_4}]}{[\overline{NO_3}]^2 \ [SO_4^=]} \qquad \text{Equation (3)}$$

Again, the unbarred bracketed terms are equivalents per liter of solution, and the barred terms are equivalents of resin bound ions per liter of resin. When Equation (3) is written in terms of equivalent fractions where

$C = [SO_4^=] + [NO_3^-]$ = sum of ion equivalents in solution

$\overline{C} = [\overline{SO_4}] + [\overline{NO_3}]$ = sum of ion equivalents on resin

then the equivalent fractions are:

$$X_s = \frac{[SO_4^=]}{C} \; ; \; X_N = \frac{[NO_3^-]}{C}$$

$$\overline{X_s} = \frac{\overline{SO_4}}{\overline{C}} \; ; \; \overline{X_N} = \frac{\overline{NO_3}}{\overline{C}}$$

Substituting in Equation (3)

$$\frac{\overline{X_s}}{(1 - \overline{X_s})^2} = K_N^S \ \frac{\overline{C}}{C} \ \frac{X_s}{(1 - X_s)^2} \qquad \text{Equation (4)}$$

Approximate selectivity coefficients are given in Table 4 (Reference 3).

TABLE 4. APPROXIMATE SELECTIVITY COEFFICIENTS FOR STRONG BASE ANION EXCHANGE RESINS

$K_N^S = 0.04$	$K_{Cl}^{HCO_3} = 0.5$
$K_{Cl}^N = 4$	$K_{Cl}^S = 0.15$
$K_{Cl}^S = 0.15$	

$S = SO_4^=$ $\quad Cl = Cl^-$

$N = NO_3^-$ $\quad HCO_3 = HCO_3^-$

Separation Factors

Clifford and Weber (Reference 2) have used the separation factor to describe the equilibrium between ions in solution and on the resin. In the case of nitrate and chloride ions

$$\text{Separation factor} = \alpha_{Cl}^N = \frac{[\overline{NO_3}]\ [Cl^-]}{[\overline{Cl}]\ [NO_3^-]} = K_{Cl}^N \qquad \text{Equation (5)}$$

in case of monovalent ions α_{Cl}^N like K_{Cl}^N is independent of concentration. However, in case of divalent ions

$$\text{Separation factor} = \alpha_N^S = \frac{[\overline{SO_4}]\ [NO_3^-]}{[\overline{NO_3}]\ [SO_4^=]} \neq K_N^S \qquad \text{Equation (6)}$$

α_N^S does not account for concentration effects as K_N^S does. K_N^S is, therefore, a more useful parameter when considering groundwaters of different or varying concentration.

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Column Effluent Profiles

Multicomponent chromatography theory (References 4, 5, 6, and 7) can be used to predict the resin phase compositions and concentration profiles of anion exchange resins. The ions removed by the resin become concentrated into enriched zones with a layering according to the resin-ion selectivity coefficients. Figure 18 shows an idealized chromatographic separation of the four major anions found in groundwater according to the usually observed resin selectivity $SO_4^{=} > NO_3^{-} > Cl^{-} > HCO_3^{-}$. The sulfate ion being the most preferred ion on the resin is able to displace all other ions (ignoring concentration effects) and thus concentrates at the inlet end of the column. The sulfate ion thus depleted by the inlet or upper portion of the resin is removed from the solution allowing the next preferred ion (nitrate) to concentrate in the next lower band. Chloride and bicarbonate concentrate in the lower portions of the column. As solution continues through the column, the zones grow and move downward with the bicarbonate the first to be eluted from the column followed in order by chloride then nitrate before sulfate breakthrough is achieved.

All anion exchangers studied by Clifford and Weber (Reference 2) have <u>average</u> sulfate-nitrate separation factors, α_N^S greater than one. Columns operated at low enough flow rates to allow equilibrium conditions to exist (and low concentrations) would therefore give the chromatographic partitioning shown in Figure 18. This partitioning may not occur, however, under conditions of high flow rates where column equilibrium is not obtained, at high sulfate to nitrate ratios for some resins, or at high anion concentrations.

The latter concentration effect is often referred to as "electroselectivity" where in dilute solutions the divalent counterions (sulfate) will be preferred

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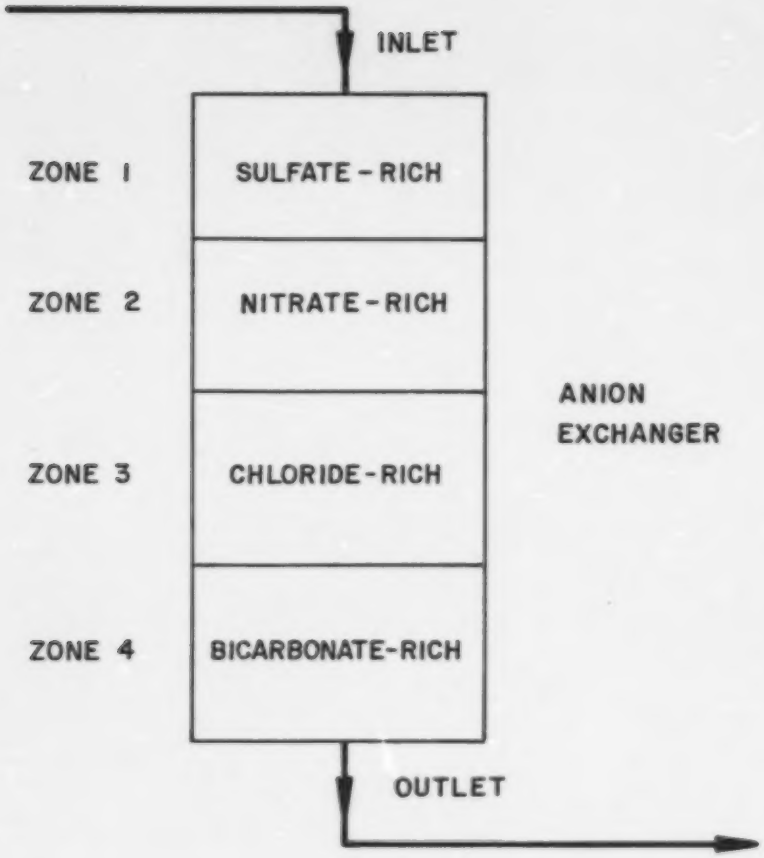

FIGURE 18. CHROMATOGRAPHIC ENRICHMENT OF GROUND WATER ANIONS IN AN EXHAUSTED ANION EXCHANGER

by the resin over a monovalent (nitrate) ion. Conversely, at high anion concentration, the monovalent ion may be preferred. As can be seen from Equation (4) when considering a mixture of sulfate and nitrate ions for the equivalent fraction of sulfate on the resin, $\overline{X_s}$, to be greater than the corresponding equivalent fraction in solution, X_s, the total anion concentration, C, must be less than 52 meq/l or approximately 2,500-ppm total anion concentration with a resin where $\overline{C}$ equals 1,300 meq/l.

$$\frac{\dfrac{\overline{X_s}}{(1-\overline{X_s})^2}}{\dfrac{X_s}{(1-X_s)^2}} = K_N^S \quad \frac{C}{\overline{C}} > 1 \qquad \text{Equation (7)}$$

$$= K_N^S \qquad \overline{C} > C$$

$$K_N^S = 0.04$$

$$\overline{C} = 1{,}300 \text{ meq/l}$$

$$C < 52 \text{ meq/l}$$

At total anion concentrations greater than 52 meq/l, the monovalent nitrate ion would be preferred by the resin and the upper band in Figure 18 would be enriched with nitrate. Sulfate would thus appear in the column eluate before nitrate ion. Although this high anion concentration will rarely occur in groundwater compositions, electroselectivity favors column regeneration when sulfate ion is to be removed. Thus sulfate is easily removed from spent columns by 1 N sodium chloride in near stoichiometric proportions.

ESTIMATION OF COLUMN PERFORMANCE

From the above resin-ion equilibria relationships, the performance of an ion exchange column for nitrate removal applications can be estimated for flow rates when equilibria can be achieved. Anderson (private communication) has developed a method for approximating the volume of water containing sulfate, nitrate, chloride, and bicarbonate which can be treated by an anion exchange resin before nitrate breakthrough is obtained. Briefly, the method is derived from the following considerations.

As discussed above in groundwaters with anionic concentrations less than 2,500 ppm, strong base anion resins show the following relative selectivities:

$$SO_4^{=} > NO_3^{-} > Cl^{-} > HCO_3^{-}$$

The column will become partitioned in zones as shown in Figure 18. As the column is eluted with a continuing flow of feed water, Zone 1 and Zone 2 will grow and expand downward until nitrate breakthrough begins to occur. Zone 1 will have a composition in equilibrium with the feed water and will contain sulfate and nitrate. Zone 2 will be in equilibrium with the water leaving Zone 1 and will contain nitrate with no sulfate. From simultaneous equations expressing sulfate and nitrate balances, the amount of nitrate on the column at the end of the run can be estimated as follows:

f = fraction of bed in Zone 1

$BV(N)$ = bed volume of effluent to nitrate breakthrough

$\overline{C}$ = capacity of resin in eq/l

a = sulfate concentration in feed meq/l

b = nitrate concentration in feed meq/l

The sulfate balances after passage of BV(N) through the column is

$$\overline{X_s}\ \ \overline{C}\ \ f = (a \times 10^{-3})\ BV(N) \qquad \text{Equation (8)}$$

The nitrate balance is

$$[(1 - \overline{X_s})\ (\overline{X'_N})\ \overline{C}f] + [\overline{X'_N}\ \overline{C}\ (1 - f)] = (b \times 10^{-3})\ \ BV(N) \qquad \text{Equation (9)}$$

Where $\overline{X'_N}$ is the fraction of the nonsulfate portion of the resin in the nitrate form in both zones. The first bracketed term represents the equivalents of nitrate in Zone 1 of the column, and the second bracketed term represents the nitrate equivalents in Zone 2. Solving the two above equations simultaneously, the following is obtained:

$$BV(N) = \frac{\overline{X'_N}\ \ \overline{C}}{a\ \overline{X'_N} + b} \qquad \text{Equation (10)}$$

$\overline{X'_N}$ represents the fraction of Zone 2 in the nitrate form as well as the fraction of the nonsulfate portion of Zone 1. The two zones will be initially established as thin sections at the top of the column. As Zone 1 grows, nitrate ion of Zone 2 is displaced and moves down the column to enrich Zone 2 in more nitrate. The nitrate concentration in equilibrium with the enriched nitrate Zone 2 will be greater than b but less than b + a.

The nitrate concentration in Zone 2, X'_N, is estimated as (b + 0.8.a). The fraction of the nonsulfate portion of the column in the nitrate form will be $\overline{X'_N}$ which is related to X'_N in Equation (11).

$$n = \frac{\overline{X'_N}}{1 - \overline{X'_N}} = K^N_{Cl}\ \ \frac{\frac{b + .8a}{C}}{1 - \frac{b + .8a}{C}} \qquad \text{Equation (11)}$$

then:

$$\overline{X'_N} = \frac{n}{1+n} \qquad \text{Equation (12)}$$

by substituting Equation (12) into Equation (10), the following is obtained:

$$BV(N) = \frac{\bar{C}}{a + b + b/n} \times 10^3 \qquad \text{Equation (13)}$$

As an example, BV(N) can be calculated from Equations (12) and (13) for Run 11078 reported in Table 3. Bicarbonate and chloride concentrations are considered as chloride

$a = 5.93$ meq/l

$b = 1.56$ meq/l

$c = 4.15$ meq/l

$K^N_{Cl} = 4$

$\overline{C} = 1.3$ eq/l

$C = 11.64$ meq/l

$$n = 4 \times \frac{\frac{1.56 + .8 \times 5.93}{11.64}}{1 - \frac{1.56 + .8 \times 5.93}{11.64}} = 4.69$$

$$BV(N) = \frac{\overline{C}}{a + b + b/n} \times 10^3 = \frac{1.3 \times 10^3}{5.93 + 1.56 + \frac{1.56}{4.69}} = 166$$

The observed experimental value for BV(N) is 157 in good agreement with the estimated value. The observed and estimated values for the column runs are discussed in the following section.

Equation (13) was used to estimate bed volumes to nitrate breakthrough for a number of water compositions. The estimates are given in Table 5.

TABLE 5. ESTIMATES OF COLUMN CAPACITY ($\overline{C}$ = 1.4 eq/l)

Concentrations in meq/l

NO_3^-	$SO_4^=$	$(\overline{Cl} + HCO_3^-) = 1$ BV(N)	$(\overline{Cl} + HCO_3^-) = 2$ BV(N)	$(\overline{Cl} + HCO_3^-) = 3$ BV(N)
1	.5	825	747	682
1	1	646	607	573
1	2	447	433	421
1	3	340	334	328
1	4	274	271	268
1	5	230	228	226
1.3	.5	696	636	585
1.3	1	563	530	501
1.3	2	405	392	380
1.3	3	315	309	303
1.3	4	258	254	251
1.3	5	218	216	214
1.6	.5	603	556	515
1.6	1	500	472	447
1.6	2	370	359	348
1.6	3	294	288	282
1.6	4	243	240	237
1.6	5	208	205	203

The chloride and bicarbonate are combined because of the similarity in the resin selectivity for these two ions. The estimates are also based on a use

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of a fully regenerated resin with a capacity of 1.4 eq/l. To determine the capacity of a column loaded with a resin with a capacity of 1.0 eq/l, the BV(N) values in the table must be multiplied by 1.0/1.4. If the resin having an anion exchange capacity of 1.4 eq/l is not fully regenerated, i.e., the equivalent fraction of resin in the nitrate form $\overline{X_N} \neq 0$, the BV(N) values listed in Table 5 must be multiplied by $(1 - \overline{X_N})$ to obtain the nitrate capacity, BV(N), of a column.

NITRATE LEAKAGE FROM INCOMPLETELY REGENERATED COLUMNS

Because it may not be practical to use fully regenerated resin columns for nitrate removal, nitrate ion will appear in the effluent from the column before the breakthrough point is obtained. The concentration of nitrate leakage from a column will depend on the total anion (chloride) concentration and the equivalent fraction of the resin in the nitrate form, $\overline{X_N}$, at the exit end of the column. Equation (2) can be used to estimate, X_N, the equivalent fraction of nitrate in the effluent. As an example, Table 6 gives values of nitrate leakage derived from Equation (2) for columns of various values of $\overline{X_N}$ with a water having a total anion concentration of 10.0 meq/l entering the column.

DISCUSSION OF RESULTS OF TWO-INCH COLUMN TESTS

Breakthrough Curves

Several tests were made using 2-inch-diameter columns with a 24-inch bed depth of resin. The test procedures are described in Section 2 of this report. The tests were conducted with Well 3 water as well as synthetic blends to determine column capacity with these waters and verify the above estimates of column capacity. Table 3 lists the results and conditions for these tests.

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TABLE 6. ESTIMATE OF NITRATE LEAKAGE THROUGH INCOMPLETELY REGENERATED COLUMNS

$\overline{X_N}$	X_N	Nitrate Leakage NO_3^- meq/l	Nitrate Leakage NO_3^- ppm
.1	.027	.27	16.7
.2	.059	.59	36.5
.3	.097	.97	60.0
.4	.143	1.43	88.7
.5	.200	2.00	124
.6	.273	2.73	169
.7	.368	3.68	228
.8	.500	5.00	310
.9	.692	6.92	429

C = Total anion concentration = 10 meq/l

K_C^N = 4

$\overline{X_N}$ = Fraction of resin in nitrate form after regeneration

Inspection of the breakthrough curves shows the formation of sulfate enriched zones only under certain conditions. Run 02199 (Figure 6) and Run 02219 (Figure 5) were both run with the same feed water composition; however, Figure 5 shows nitrate breakthrough occurring well before sulfate breakthrough along with a nitrate peak above the influent concentration. This breakthrough pattern is to be expected when a sulfate enriched zone is formed at the top of the column and a nitrate enriched zone is formed at the bottom as discussed in the above section. As the sulfate enriched zone grows after nitrate breakthrough, sulfate ion displaces the resin-bound

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nitrate in the nitrate zone. The nitrate effluent concentration will exceed the influent concentration because of this displacement by sulfate. A different effluent profile is obtained with the Type II resin, A-104, in Run 02199 which shows a nearly simultaneous breakthrough for nitrate and sulfate ions indicating that the enriched sulfate and nitrate zones do not occur at these concentrations. This indicates the selectivity under these conditions for Type I resin is $SO_4^= > NO_3^-$ and for Type II resin is $SO_4^= = NO_3^-$. In Run 03059 (Figure 7) with the Type II resin, sulfate ion breakthrough occurs before nitrate. Run 03299 (Figure 8) shows the same behavior as A-104 resin. Resins A-101D, A-104, and Dowex SAR are of the microporous type. When the macroporous resins are compared, nitrate and sulfate breakthrough occurred nearly simultaneously without nitrate effluent concentration exceeding the influent concentration for both Type I and Type II resins (Runs 06229 and 06279, Figures 9 and 10). Thus indicating that chromatographic partitioning does not occur with the macroporous resins at these concentrations.

Run 02290 (Figure 11) with A-101D resin showed nitrate breakthrough prior to sulfate, but the rise of effluent nitrate concentrations above influent concentration is not as apparent as in Run 02219. Run 03050 (Figure 19) shows the typical breakthrough pattern of the A-101D resin, however, Run 03140 (Figure 20) does not which can be attributed to nonequilibrium at high flow rates.

The conditions under which chromatographic partitioning did or did not appear as indicated by column effluent profiles are compared in Table 7. Only one resin, A-101D, has thus far exhibited an effluent pattern suggestive of chromatographic separation. At flow rates above 0.33 BV per minute (Runs 02260, 02230, and 03140), the chromatographic pattern either does

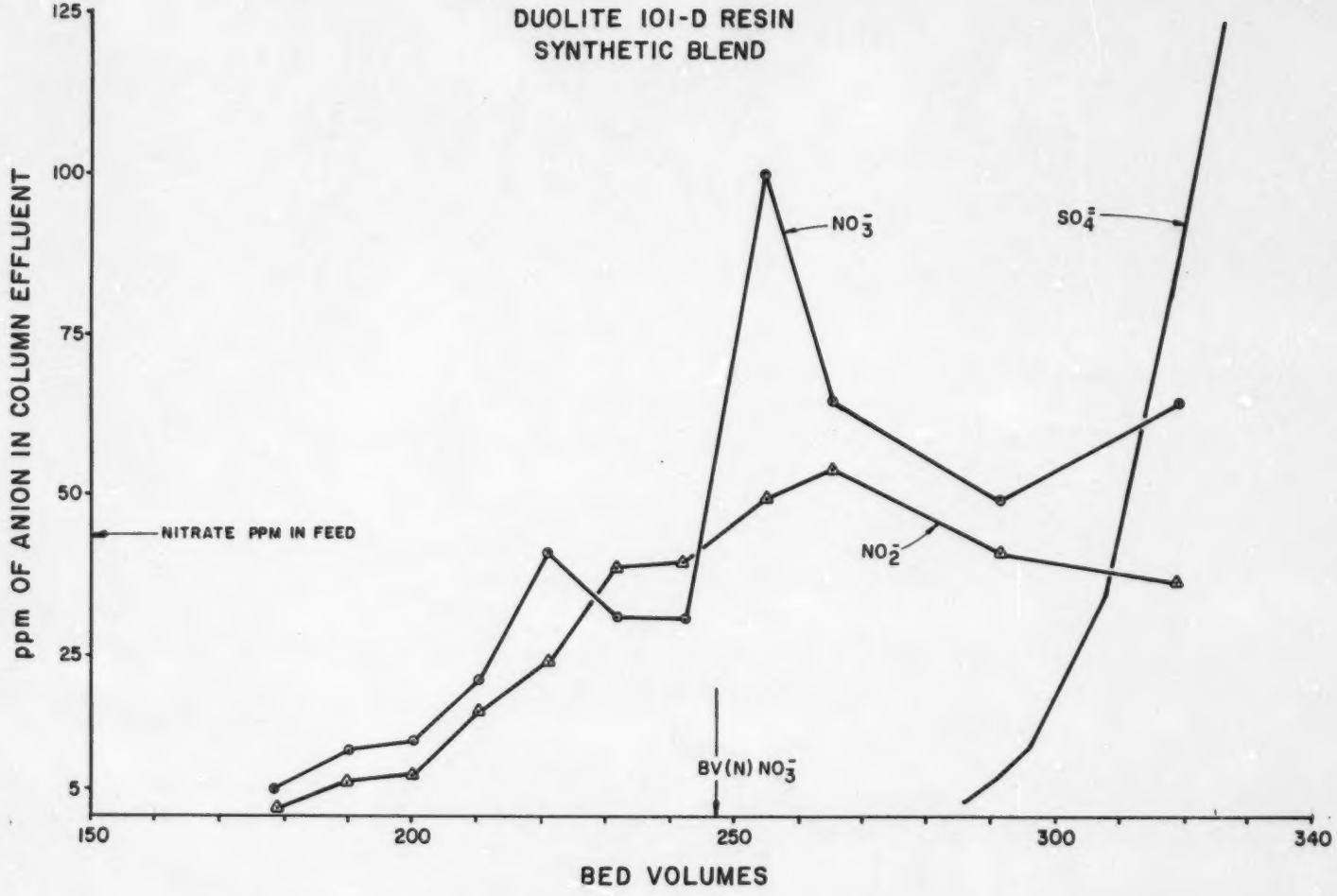


FIGURE 19. ION EXCHANGE COLUMN EXPERIMENT 03050

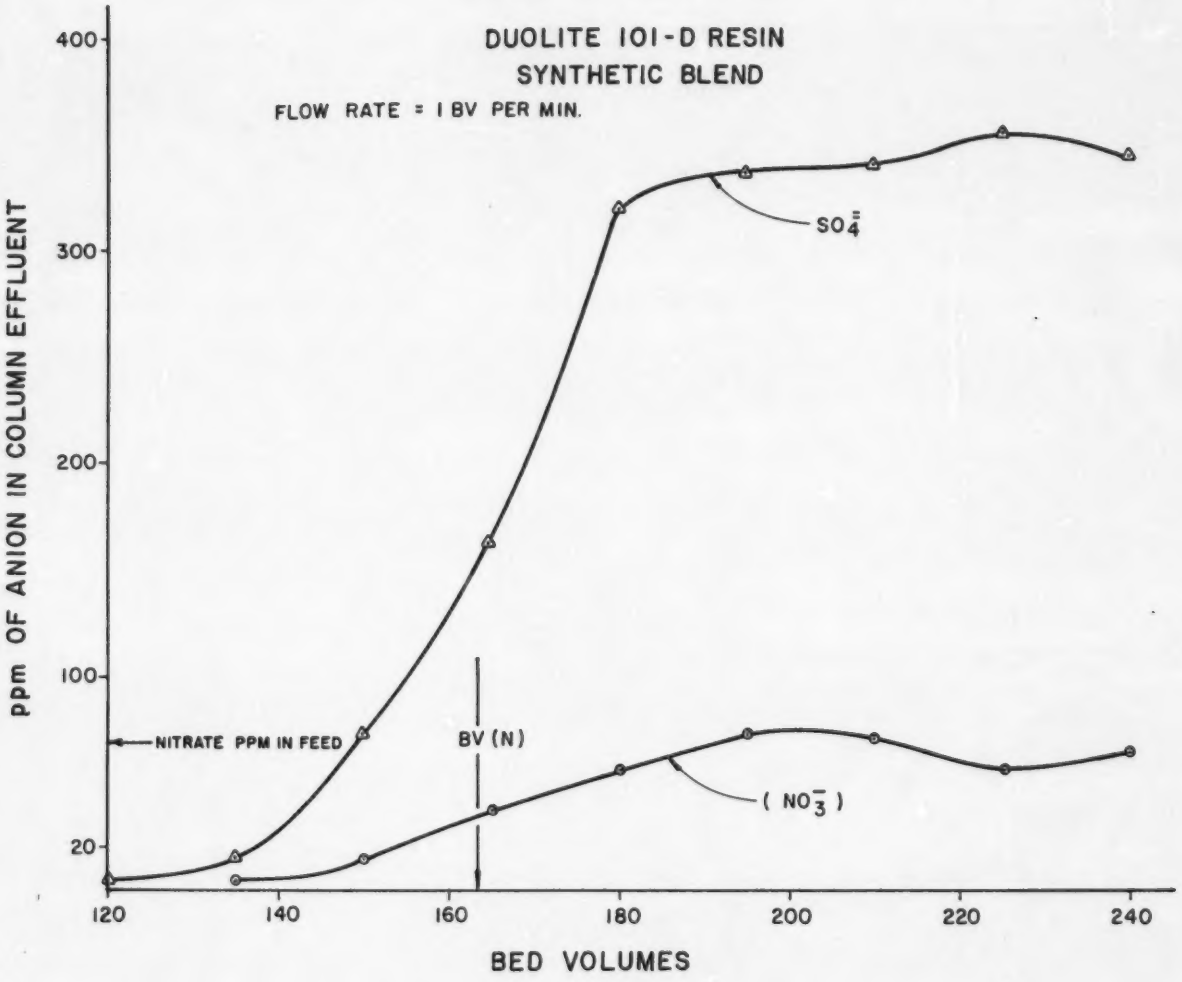


FIGURE 20. ION EXCHANGE COLUMN EXPERIMENT 03140

TABLE 7. COMPARISON OF COLUMN EXPERIMENTS

Run No.	Effluent Pattern Suggestive of Chromatographic Partitioning	Resin (Type)	Resin Porosity*	meq $SO_4^=$	meq NO_3^-	$\frac{\text{meq } SO_4^=}{\text{meq } NO_3^-}$	Flow Rate BV/min
11078	--	A-101D(I)	micro	5.93	1.56	3.81	.33
02199	no	A104(II)	micro	4.69	1.11	4.23	.33
02219	yes	A-101D(I)	micro	4.69	1.11	4.23	.33
03059	no	A104(II)	micro	6.70	1.92	3.49	.33
03299	no	A104(II)	micro	7.65	1.74	4.40	.33
06229	no	IRA-900(I)	macro	7.18	1.80	3.99	.33
06279	no	IRA-910(II)	macro	7.18	1.80	3.99	.33
02290	yes	A-101D(I)	micro	7.33	1.71	4.29	.36
02260	no	A-101D(I)	micro	7.75	1.26	6.15	1.10
02230	no	A-101D(I)	micro	6.87	1.49	4.61	1.56
03050	yes	A-101D(I)	micro	3.64	1.63	2.23	.33
03140	no	A-101D(I)	micro	8.33	1.12	7.43	1.00
03069	yes	A-101D(I)	micro	3.35	0.85	3.94	.33

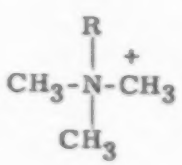
*Duolite 101D has a moisture content of 48 to 55 percent; Duolite A104 has moisture content of 40 to 46 percent; Dowex SAR moisture content equals 38 to 45 percent; IRA-900 has a moisture content of 60 to 64 percent; and IRA-910 has a moisture content of 50 to 55 percent.

not occur or is distorted by high flow rates. These results can be correlated with the isotherm data obtained by Clifford (Reference 2).

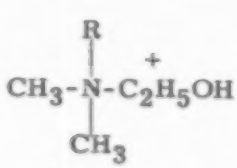
Figures 15, 16, and 17 show isotherms for three of the resins tested. For the IRA-900 resin, an S-shaped isotherm is quite obvious indicating that

at high sulfate equivalent fractions, the resin becomes more selective for nitrate than sulfate. Similar but less pronounced S shape of the isotherm for A-104 resin is also shown, Figure 16. Thus it is reasonable that these two resins would not show the effluent pattern suggestive of chromatograpic partitioning at these high sulfate concentrations but show diminished or equal sulfate over nitrate selectivity. The isotherm for A-101D, Figure 15, does not show the S-shaped isotherm, therefore, the resin is able to retain the sulfate over nitrate selectivity at the high sulfate concentrations.

These limited results indicate that the differences between A-104 and A-101D may be significant in considering sulfate to nitrate selectivity. The difference between the two resins is one of moisture content, degree of cross linking and the type of pendant groups on the quaternary nitrogen as shown below:



Type I
A-101D



Type II
A-104

Resins having varied pendant groups are being synthesized and will be column tested for nitrate selectivity. Previous work (Reference 2) has indicated that the kind of substituents on the functional amine group is one of several factors which can influence the nitrate to sulfate selectivity. For example, the higher the amine (secondary, tertiary, or quaternary), the less selectivity for sulfate over nitrate. No apparent effect was noted on nitrate to chloride selectivity for those amines. However, it is not possible to predict

either how or to what extent specific structural changes about the quaternary nitrogen will influence nitrate selectivity.

Column Capacity

The column capacity for nitrate removal can be estimated from the composition of the feed water and compared to the experimentally obtained values. Bed volumes to nitrate breakthrough BV(N) were estimated from Equation (13) and compared to the experimentally obtained values. These are compared in Table 8.

Equation (13) gives the best estimates for the A-101D resin if results of runs made at high flow velocity are ignored because of the nonequilibrium conditions. For this resin, the average deviation of the experimental value from the estimated value is ±4.45 percent. The A-104, Dowex SAR, IRA-900, and IRA-910 all give higher experimental values than the estimated value. Equation (13) was derived for those cases where chromatographic partitioning of sulfate and nitrate occur on the resin column. It is therefore a good estimate for those cases but can be as much as 30 percent too low for the other resins which were studied. It is interesting to note that at high flow velocities with the A-101D resin, Equation (13) can give estimates 20 percent too low. This must be attributed to kinetic effects in the complex reacting system.

Columns where partitioning of sulfate and nitrate do not occur but form a zone homogeneous in nitrate and sulfate can be estimated using different relationships. Assuming that nitrate and sulfate ions are absorbed on the resin in preference to chloride and bicarbonate, an estimation of column capacity can be made by considering these ions alone:

$$BV(N) = \frac{\bar{C}}{\text{meq } SO_4^{=} + \text{meq } NO_3^{-}} \qquad \text{Equation (14)}$$

TABLE 8. ESTIMATION OF COLUMN CAPACITY USING EQUATION (13)

Run No.	BV(N) Experimental	BV(N) Estimated Equation (13)	Percent Deviation $\frac{\text{Estimate-Experimental}}{\text{Estimate}} \times 100$
11078	157	166	+5.42
02199	240	229	-4.80
02219	198	210	+5.71
03059	172	154	-11.69
03299	184	143	-28.67
06229	140	106	-32.07
06279	122	106	-15.09
02290	147	149	+1.34
02260*	159	140	-13.57
02230*	176	150	-17.33
03069	300	289	-3.81
03050	248	234	-5.98
03140*	163	135	-20.74

*Runs made at high flow velocity.

Estimates based on Equation (14) are given in Table 9. Again, if runs at high flow rates are discounted, the average deviation for all other runs is $\pm$7.2 percent.

It should be pointed out that the water compositions thus far investigated in this work are high in sulfate content. Use of Equation (13) should apply to waters of low sulfate concentration because it includes the effect of chloride and bicarbonate ions. Equation (14) does not and will not apply to solutions

TABLE 9. ESTIMATION OF COLUMN CAPACITY USING EQUATION (14)

Run No.	BV(N) Experimental	BV(N) Estimated Equation (14)	Percent Deviation $\frac{\text{Estimate-Experimental}}{\text{Estimate}} \times 100$
11078	157	173	+9.2
02199	240	241	+0.4
02219	198	221	+10.4
03059	172	162	-6.2
03299	184	149	-23.5
06229	140	123	-13.8
06279	122	123	+0.8
02290	147	153	+3.9
02260*	159	144	-10.4
02230*	176	156	-12.8
03069	300	309	2.9
03050	248	246	-0.8
03140*	163	138	-18.1

*Runs made at high flow rates.

and bicarbonate ions. Equation (14) does not and will not apply to solutions of low sulfate where chloride and nitrate are present. Data from Clifford and Weber (Reference 2) for Ionac AFP-100 (a Type I resin) is as follows:

Resin Capacity meq/l = 1.07

HCO_3^-	= 1.0 meq/l
Cl	= 1.5
NO_3^-	= 1.5
$SO_4^=$	= 1.5
BV(N)	= 295 experimental
BV(N)	= 316 Equation (13); % deviation = 6.6
BV(N)	= 357 Equation (14); % deviation = 17.4

SECTION 5

RESULTS OF ION EXCHANGE PILOT COLUMN TESTS

INITIAL TEST RUNS - MODE A OPERATION

The installation of the HI-FLO 5 System was previously described. Operation of the system was initiated on May 31, 1979, without any further modification using Well 3 water of the following composition:

NO_3^- meq/l	= 1.80
HCO_3^-	= 2.50
Cl	= 2.82
$SO_4^=$	= 7.18

Bed capacity is estimated as

BV(N)	= 139 Equation (13)
BV(N)	= 145 Equation (14)

Initial test conditions are referred to as Mode A operation and were as follows:

Mode A

Program Sequence

Service	- 11.74 gpm to breakthrough.
Backwash	- 10 gpm for 10 minutes.
Brine Rinse	- Variable from 20 to 40 minutes. Determined by quantity of water put into brine tank.

Slow Rinse - 55 minutes minus brine rinse time.

Conditioning Rinse - 10 gpm for 10 minutes.

Other Conditions

Brine Concentration - Approximately 12 percent.

Brine and flow distributor provided by vendor.

The breakthrough curve for virgin resin exhaustion gave BV(N) = 125 BV of treated water. Some nitrate leakage was detected during exhaustion on the first and subsequent runs indicating hydraulic leakage or channeling. Salt dosage was varied by lengthening the brine tank refill time and/or adding extra water to the brine tank.

In this particular mode, the system was operated to exhaust the resin and regenerate on alternate days. Data obtained from the first series of runs are given in Table 10. Salt dosages listed in Table 10 show no effect on bed capacity or nitrate level in product water. Performance indicated that treatment of 123 BV (4,011 gallons) would require about 121 pounds of salt (27.8 pounds salt per cubic foot of resin).

Operation of the pilot column was continued in Mode A to generate data in Figure 21 which shows nitrate leakage at various levels of salt dosages used for regeneration. Because of the high salt dosage requirements, the mechanical and hydraulic design of the pilot column was closely examined to seek more efficient operation.

MODIFICATION OF PILOT COLUMN AND MODE B OPERATION

As received from the vendor, the HI-FLO 5 had a 1-1/2-inch inlet pipe at the top of the ion exchange tank as shown in Figure 22 (a). This was modified as shown in Figure 22 (b) using 1-inch PVC fittings and pipes to give a

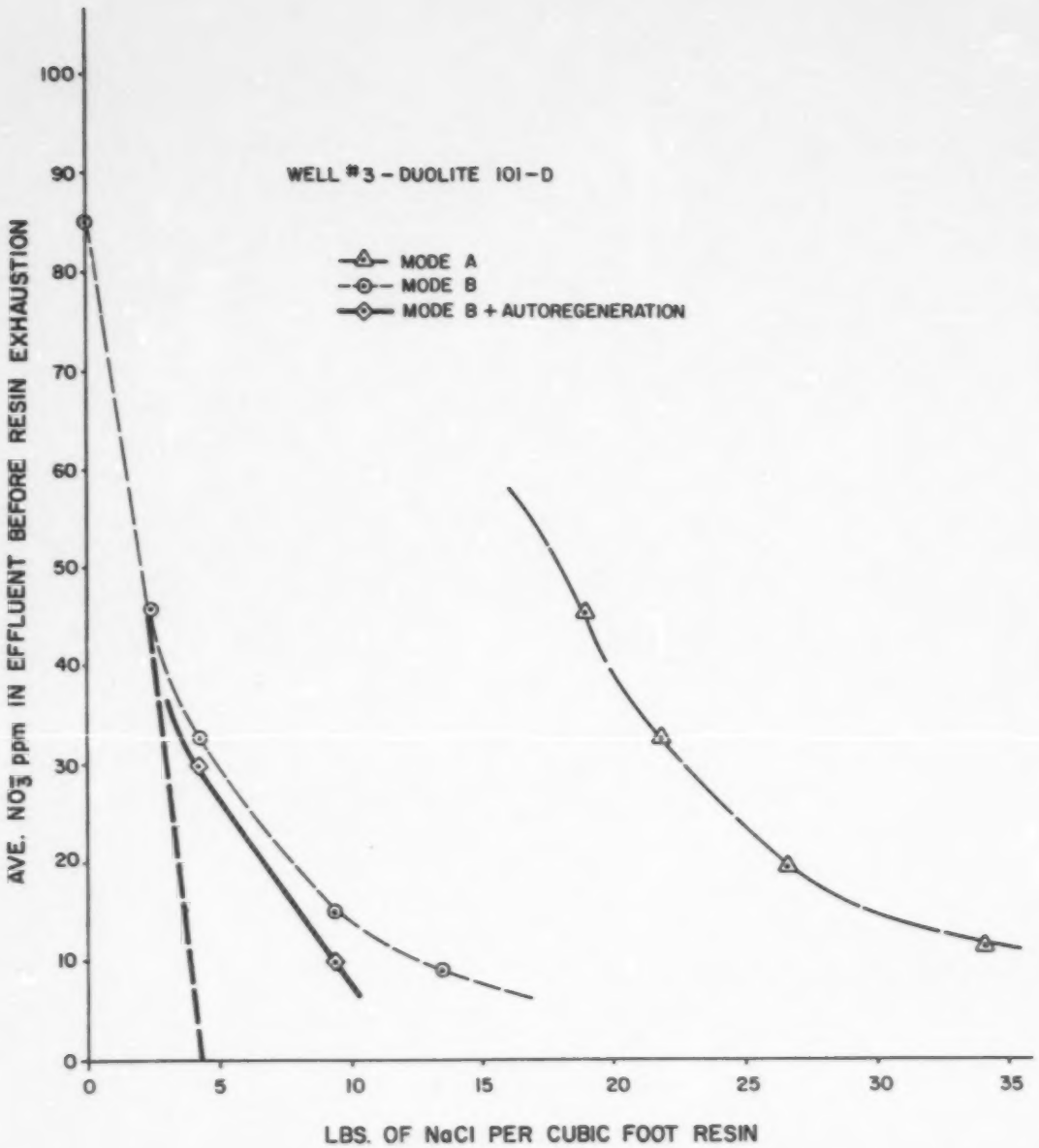


FIGURE 21. PILOT COLUMN ION EXCHANGE SYSTEM NITRATE LEAKAGE DEPENDENCE ON MODE OF OPERATION AND SALT LOADING

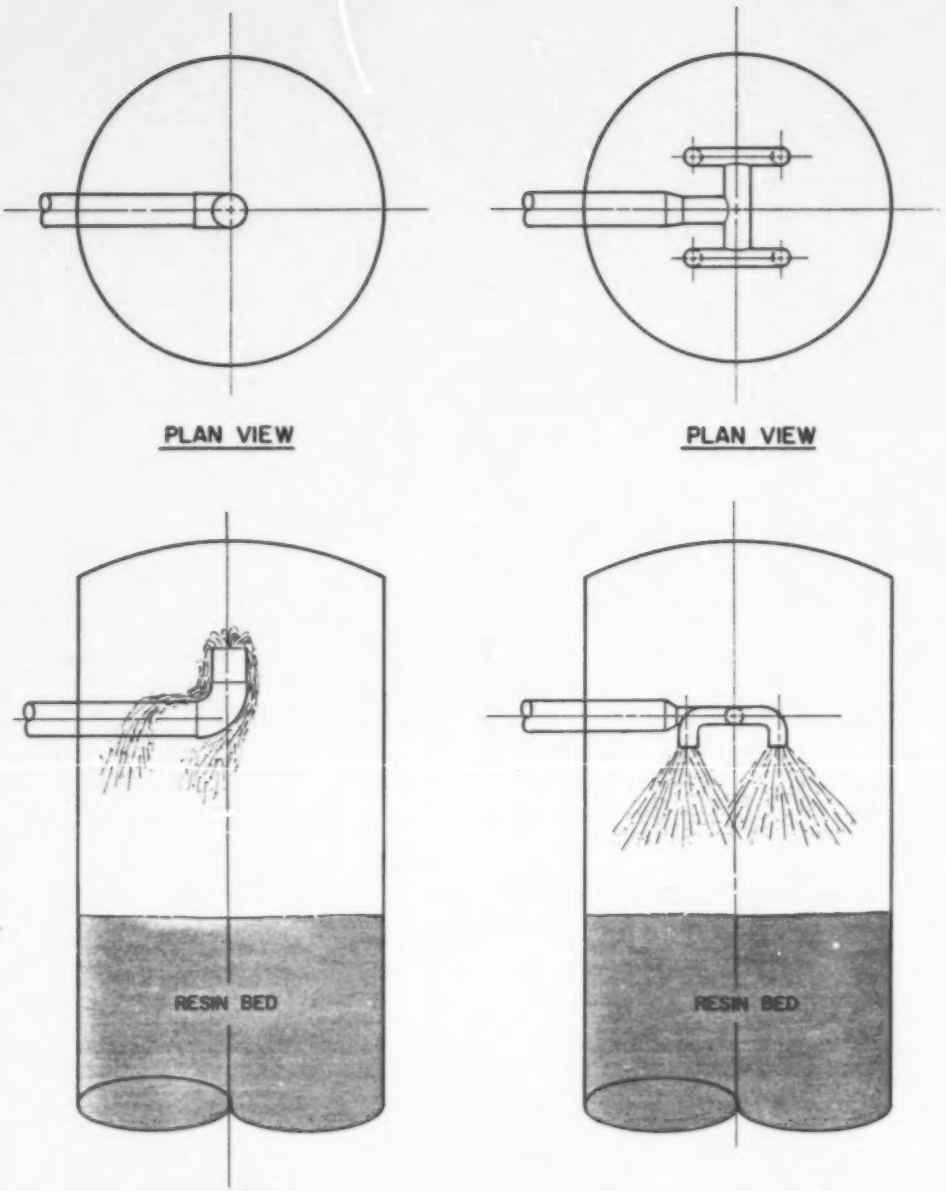


FIGURE 22. FLOW DISTRIBUTION IN VENDOR SUPPLIED SYSTEM (a) AND MODIFIED SYSTEM (b)

TABLE 10. ANION EXCHANGE PILOT COLUMN DATA

Run No.	Estimate of Salt Dosage (lb/cu ft)	Bed Volumes to NO_3^- Break	Highest ppm NO_3^- in Product
05319	Virgin	125	8.8
06059	27.7	108	--
06079	27.7	123	19
06139	36.9	124	15
06189	36.9	127	18
06209	36.9	127	13
06229	33.4	117	20
06269	33.4	127	9
07019	33.4	132	25

four-point flow distribution at the top of the column. It is believed that at the low flow rates of the dense brine (12 percent), the configuration in Figure 22 (a) promoted channeling around the resin bed by allowing the denser solution to rapidly flow to the bottom of the bed.

The operation was also modified to give a less dense brine (ca 3 to 6 percent) and declassify (evenly distribute) the bed after regeneration. As previously discussed, the A-101D resin forms an enriched sulfate zone at the top of the column and a nitrate rich zone at the bottom of the column.

This separation is suited for downflow regeneration since the nitrate is already at the exit end of the column thus obviating the necessity to move nitrate from top to bottom (as would be required by upflow regeneration). Incomplete regeneration would then leave a nitrate rich resin zone at the exit

of the column from which high nitrate leakage could occur. The program sequence was thus changed to regenerate before backwashing. Backwashing was also done intermittently to aid in declassifying the enriched zones of the bed.

The operation was also modified to give the slowest rate of brine draw which could be achieved with this system. Brine draw rate was reduced to give 3 to 6 percent salt content after mixing with eductor water. To accomplish this, a manually operated shutoff valve was installed in the brine line to control the amount of time that the brine could be drawn into the eductor. This provided a positive control over brine flow into the system. Salt dosage per run could be measured by the fall in brine level in the brine tank and measurement of salt content of the brine. Since this brine draw rate proved to be quite constant, timing the period of brine draw was also used to control the salt dosage.

Mode B operation of the pilot column was set as follows:

Mode B

Program Sequence

Service	- 12 to 45 gpm to breakthrough.
Brine Rinse	- Variable by manually opening and closing valve in brine line; varied in pilot plant from 7.5 to 45 minutes at 5 BV per hour.
Slow Rinse	- 45 minutes at 3 gpm.
Conditioning Rinse	- 10 gpm for 10 minutes (intermittent to declassify resin).

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Other Conditions

Brine Concentration - 3 to 6 percent.

Brine flow distributor redesigned as described in text (Figure 22 [b]).

A comparison of the performances of the two different modes of operation is given in Figure 23. Nearly equivalent performances are obtained operating in Mode A with 22 pounds of regenerant per cubic foot of resin and Mode B with 4.5 pounds of regenerant per cubic foot of resin. This represents an 80 percent reduction in salt requirements. Increasing the salt loading to 13.5 pounds and operation in Mode B gives slightly longer bed life and a much lower nitrate leakage.

In these cases, the bed does not become completely regenerated as is indicated by the nitrate leakages and the shorter bed lives as compared to laboratory column experiments reported above.

A further comparison of several pilot column runs using the two modes of operation is shown in Figure 21. In Mode A operation, salt load requirements are consistently higher for equivalent nitrate leakages found for Mode B. For very low salt loadings on the Mode B curve, a rapid drop in nitrate leakage is shown for small increases in salt loading. Extrapolation of the slope (heavy dashed line) intercepts at a salt loading of 4.7 which corresponds to one equivalent of resin being regenerated by one equivalent of salt. This indicates that sulfate is being removed stoichiometrically and occurs in the early portion of the regeneration period. The curved portion of the Mode B curve represents nitrate removal. In two runs of Mode B operation, the system was allowed to operate past the breakthrough point and allow the resin to "autoregenerate" or allow sulfate to accumulate and throw

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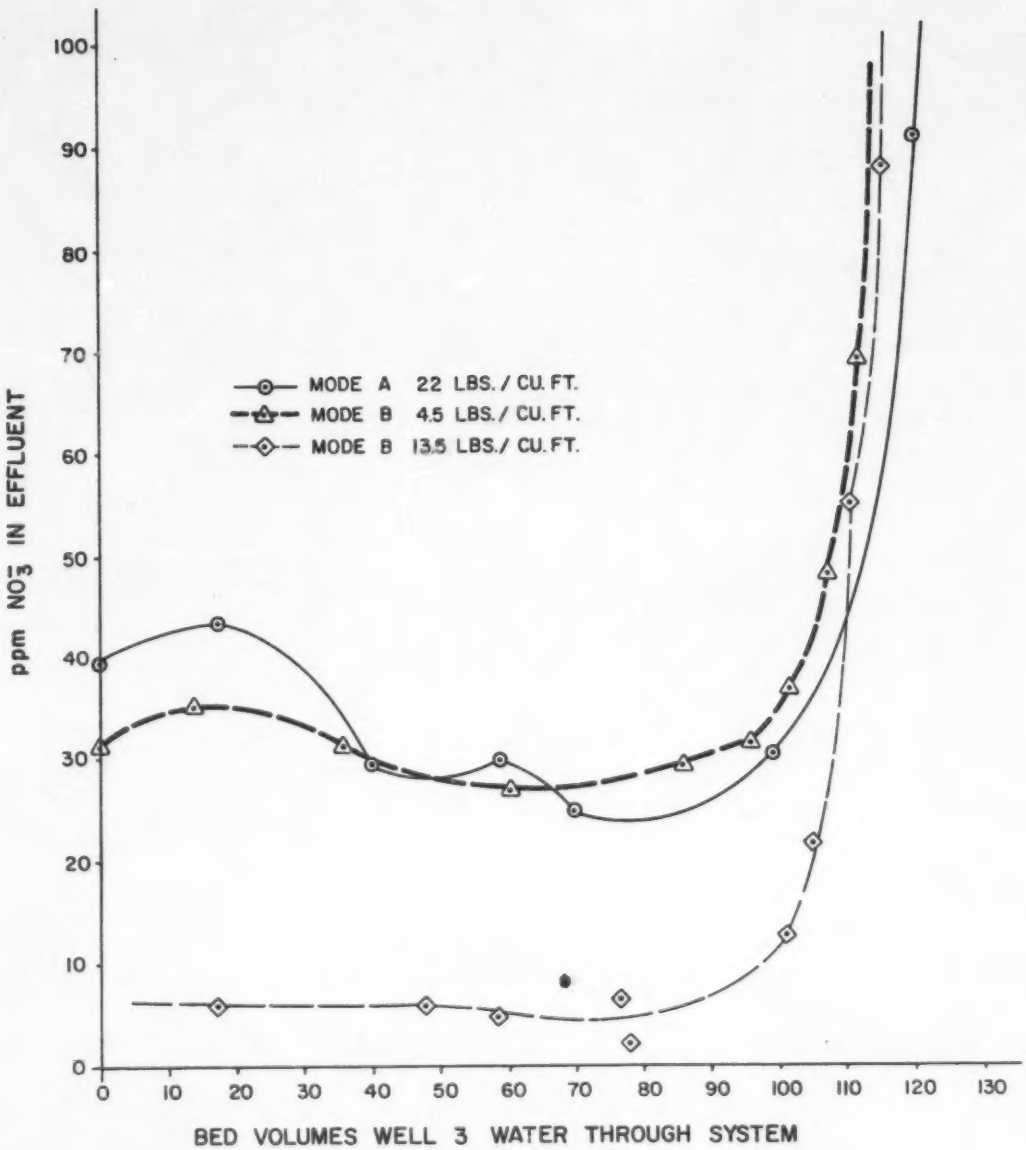

FIGURE 23. PILOT COLUMN ION EXCHANGE SYSTEM - BREAKTHROUGH CURVES WELL NO. 3 DUOLITE 101-D

off excess nitrate. (This also simulates partial regeneration by an R.O. brine.)

It is seen that salt savings can be realized when regenerating the nitrate portion of the bed after "autoregeneration." For example, to operate the system to give a nitrate leakage of 7.5 ppm, the salt loadings would be:

Mode	Salt Loading (lb/cu ft)
A	Over 35
B	15
B+ autoregeneration	9.5

This data indicates that regeneration by an R.O. brine from Well 3 offers a potential savings of 37 percent in salt requirements at this level of nitrate leakage.

This suggests that the main plant for nitrate removal would be an ion exchange system. Addition of an R.O. system would be useful for brine generation to reduce regenerant salt requirements. A bonus would be blending of R.O. product back into the process stream to reduce sulfate and TDS loads on the resin as well as providing a lower TDS in product water.

WASTE BRINE COMPOSITION

Samples of waste brine were analyzed for nitrate and sulfate during Mode B regeneration runs with the pilot column. The resin was rinsed with 6 percent brine for a period of 82 minutes to promote complete nitrate removal. Sulfate and nitrate concentrations are plotted in Figure 24 versus BV of waste brine leaving the system. No samples were taken until 1 BV had been discharged from the system. The first BV of brine into the system

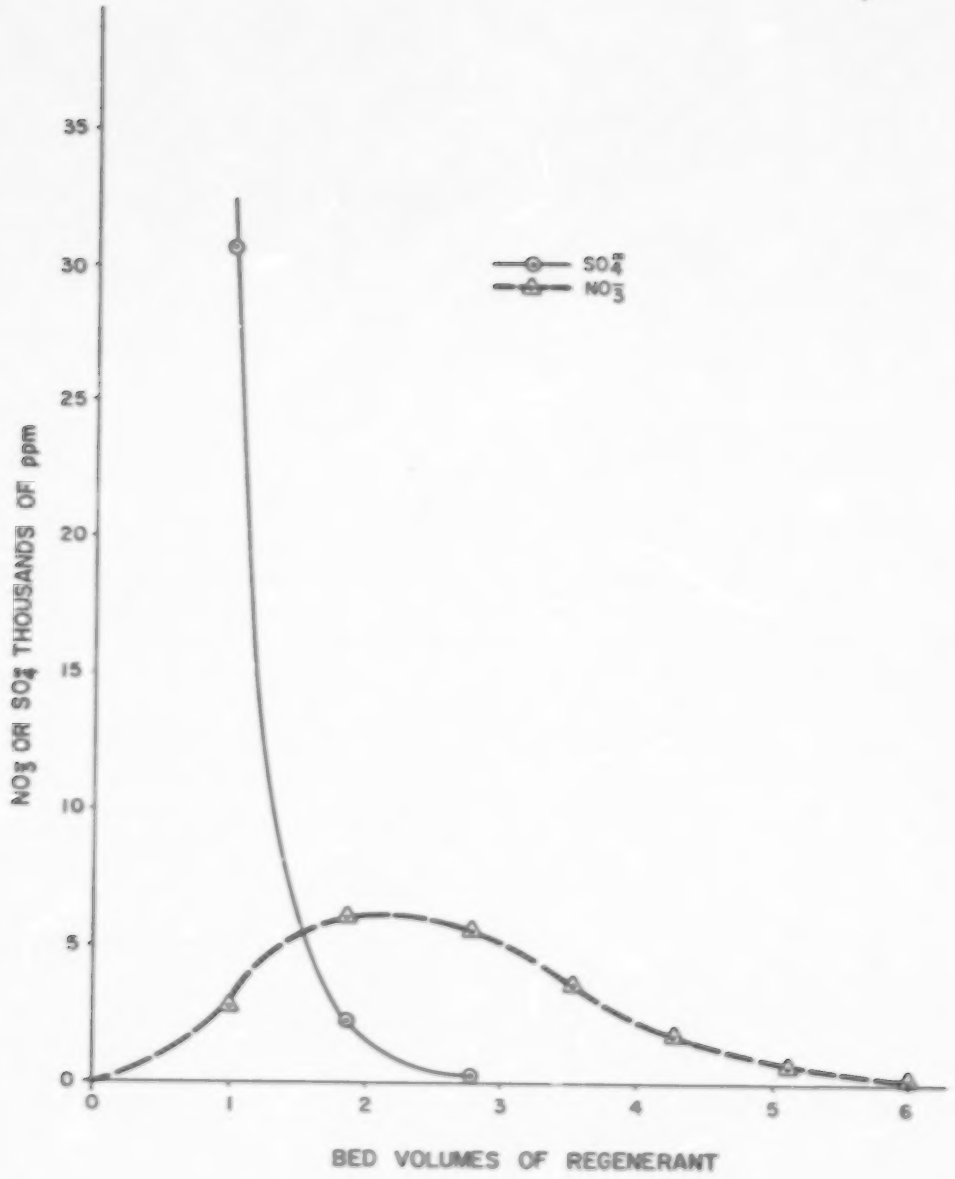

FIGURE 24. SULFATE AND NITRATE IN 6% BRINE DISCHARGE FROM SYSTEM

becomes diluted with the water above the resin bed. Full-strength brine was not obtained until the second BV was discharged. However, it can be seen that the first BV discharged was very high in sulfate ion. It appears again that sulfate is efficiently removed by the brine (approximately 1.5 BV). The regeneration capacity of the brine in the first BV is consumed by sulfate removal and is not effective in removing nitrate.

Planimeter measurements of area under the nitrate curve give the following nitrate removals per BV:

Bed Volume of Brine Discharged From System	% Nitrate Removed by Each Bed Volume	Cumulative Percentage of Nitrate Removed
1st	3.26	3.26
2nd	30.44	33.70
3rd	38.04	71.74
4th	19.13	90.87
5th	6.96	97.83
6th	2.17	100.00

Also from integration of the nitrate curve, it is estimated that 36.6 equivalents of nitrate were removed in 6 BV. This represents 23 percent of the resin bed capacity.

FLOW RATE STUDIES

It is economically advantageous to operate ion exchange columns at high flow rates to reduce the cost of capital equipment and resin quantity.

A series of short-term exploratory runs were made to determine the effect of flow rate during the service cycle. The system was operated in regeneration Mode B as described above. The data for these runs are given

in Table 11. Flow rates were varied from approximately 4 to 10 gpm per square foot. Each time, the resin was regenerated in regeneration Mode B with 4.48 pounds of sodium chloride per cubic foot of resin. This level of regeneration was chosen because it is believed that the resin is more sensitive to flow rate in a state of partial regeneration. Data suggested that the lowest nitrate leakage was obtained with the highest flow rate which was not expected.

TABLE 11. ION EXCHANGE PILOT COLUMN EFFECT OF SERVICE FLOW RATE ON NITRATE LEAKAGE[a,b]

Flow Rate (BV/hr)	Flow Rate (gpm/sq ft)	Average Nitrate Leakage (ppm)
39.7	9.9	38.1
32.0	8.0	47.6
18.4	4.6	41.6
16.8	4.2	42.4
16.4	4.1	42.8
20.3	5.1	43.5
20.4	5.1	40.6
20.6	5.1	40.0
23.6	5.9	46.1
23.6	5.9	45.5
25.8	6.4	48.8

[a] Regeneration Mode B with 4.48 lb/cu ft resin.
[b] Well 3 nitrate = 87 ppm.

A longer series of tests was then made to further investigate the effects of higher flow rates. Two-inch IPS pipe was installed as the inlet and outlet to the Hi-FLO 5 to allow flow rates higher than 10 gpm. A 1-inch water meter was also installed.

The results of 31 tests given in Table 12 show no loss of column efficiency at the highest obtainable flow rate of 1.38 BV per minute (6.02 gallons per cubic foot of resin or 22.5 gpm per square foot of resin). Breakthrough curves for representative runs are shown in Figures 25 through 28.

COMPARISON OF PILOT COLUMN TESTS WITH ESTIMATES OF PERFORMANCE

Method

The regenerant requirements for any given nitrate leakage through a column of resin and for treatment of unit quantity of water can be estimated in the following steps:

Step 1 - Estimate maximum column capacity.

Step 2 - Estimate residual nitrate on exhausted resin.

Step 3 - Estimate quantity of water treated to nitrate breakthrough at given nitrate leakage.

Step 4 - Estimate regenerant requirements.

This method is illustrated below using McFarland Well 3 water and A-101D resin. Although the method is applicable for other water compositions and other strong base anion exchange resins, only pilot column data has been obtained for Well 3 compositions and the particular resin used.

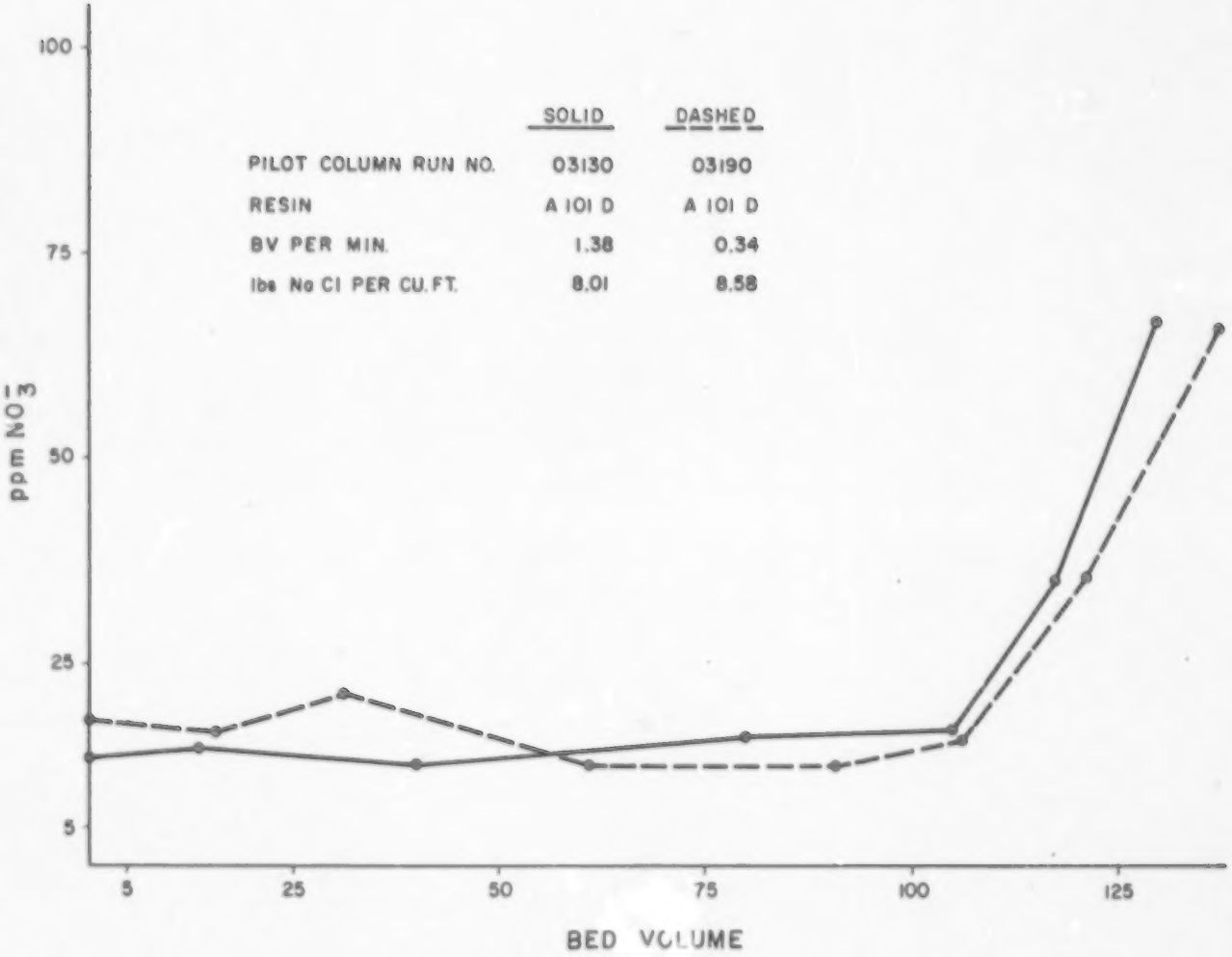

FIGURE 25. PILOT COLUMN RUNS - EFFECT OF FLOW RATE

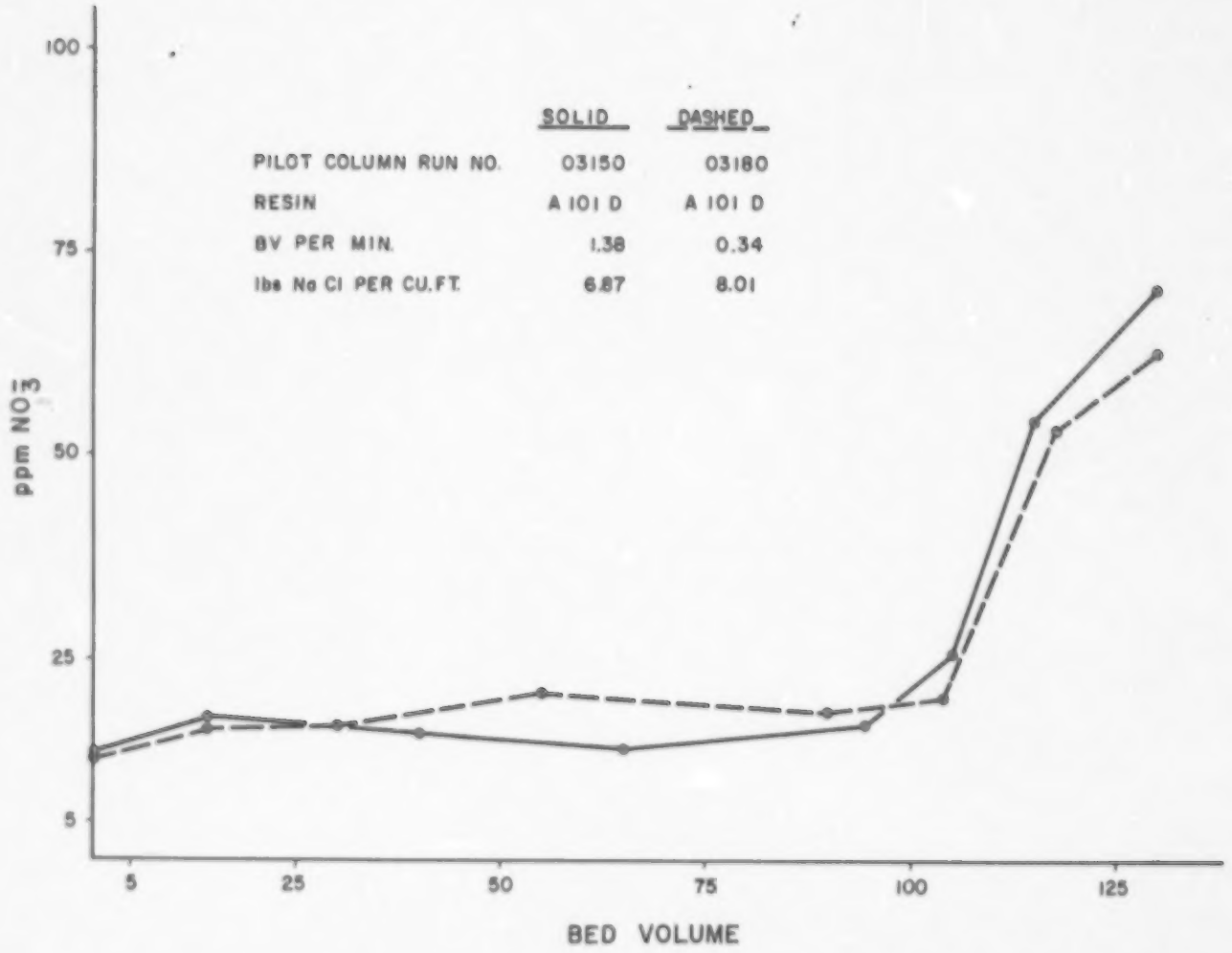

FIGURE 26. PILOT COLUMN RUNS - EFFECT OF FLOW RATE

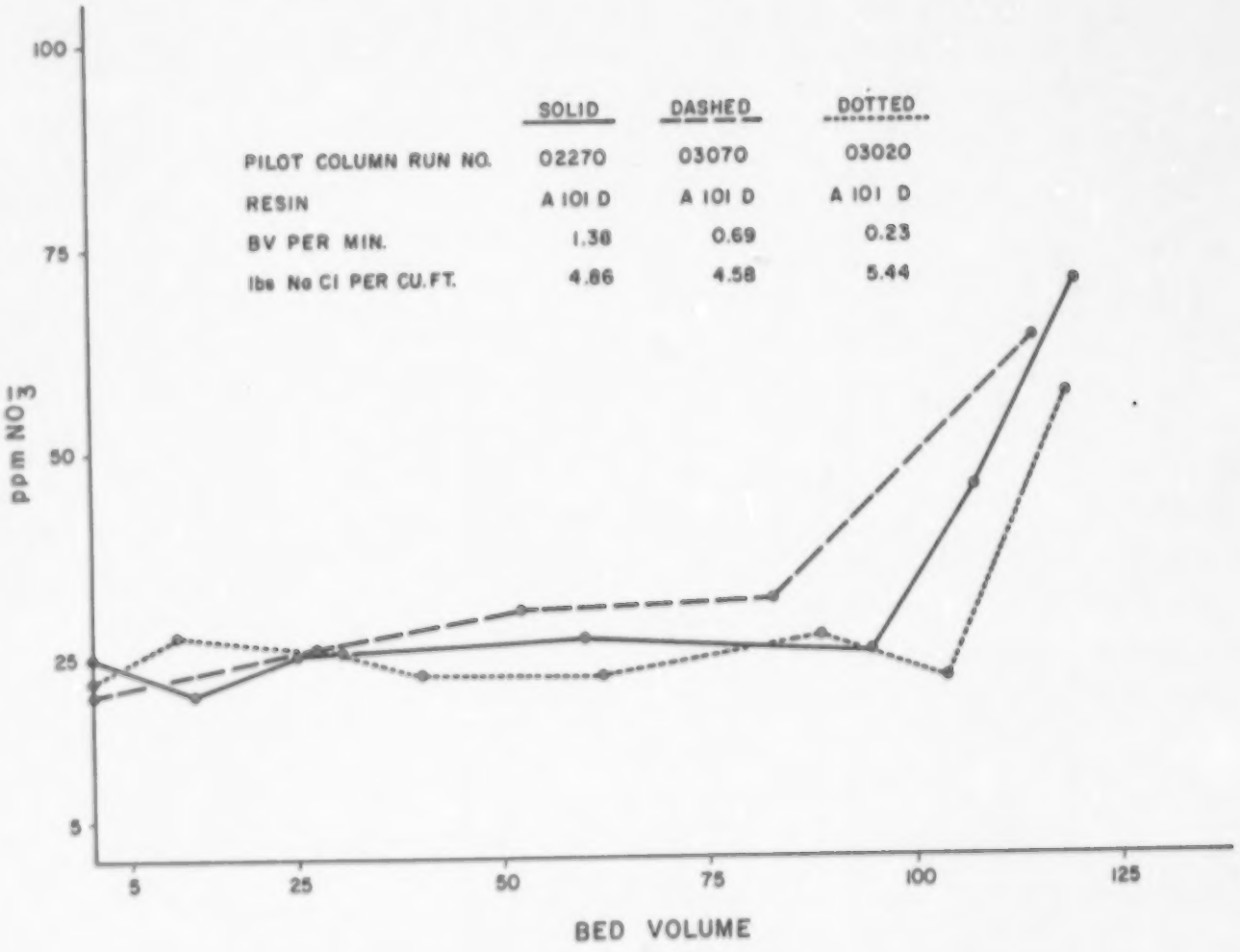

FIGURE 27. PILOT COLUMN RUNS - EFFECT OF FLOW RATE

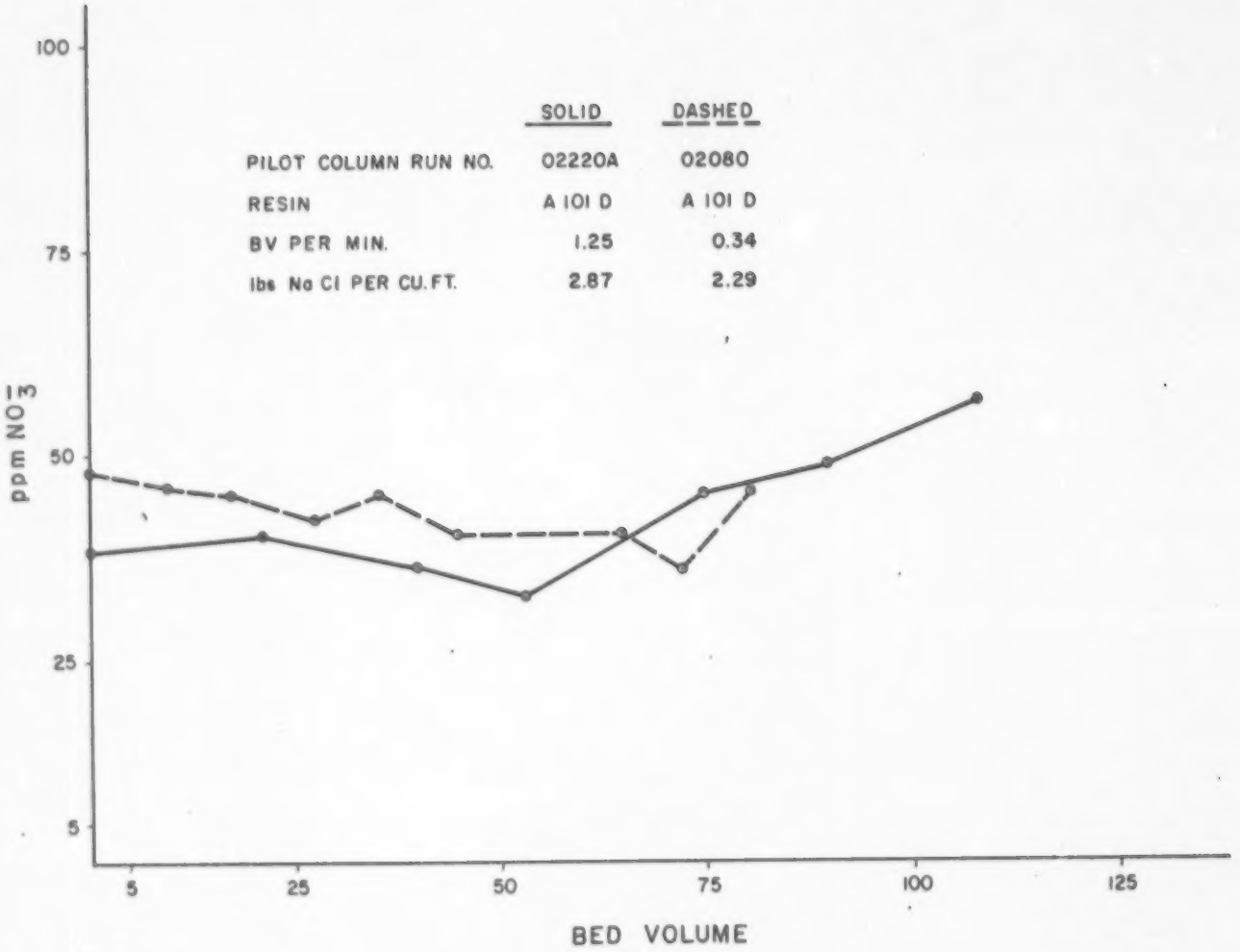

FIGURE 28. PILOT COLUMN RUNS - EFFECT OF FLOW RATE

TABLE 12. PILOT COLUMN DATA

Run No.	BV/Min	Regenerant (lb NaCl/ft^3)	Average NO_3^- Leakage (ppm)	BV(N)	Figure No.
01220	0.63	2.29	40	72	
01220A	0.63	2.58	38	72	
01240	0.63	2.29	40	81	
01280	0.34	2.29	50		
01280A	0.34	2.29	37	64	
01300	0.34	2.29	45		
01300A	0.34	2.58	37	53	
02060	0.34	2.29	43	42	
02080	0.34	2.29	45	80	28
02120	0.34	2.00	48		
02180	0.23	2.29	44	75	
02210	1.15	2.15	45	65	
02220	1.38	1.72	55		
02220A	1.25	2.87	43	75	28
02250	1.38	2.29	44	75	
02260	1.38	4.86	30		
02270	1.38	4.86	29	108	27
02280	1.38	5.72	25	108	
02290	0.34	4.86	27	90	
02300	0.34	4.86	25	92	
03020	0.23	5.44	28	114	27
03030	0.23	5.72	28	113	
03070	0.69	4.58	30	97	27
03070A	0.69	4.58	30	97	
03120	1.38	8.01	24	120	
03130	1.38	8.01	15	122	25
03140	1.38	8.01	25	127	
03150	1.38	6.87	18	112	26
03180	0.34	8.01	20	114	26
03190	0.34	8.85	15	127	25
03210	0.34	7.44	18	124	

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Maximum Column Capacity - Step 1

Estimates of maximum column capacity for completely regenerated columns can be made using Equation (13) or Equation (14) for McFarland Well 3 of the following composition with resin having an exchange capacity of 1.3 eq/l:

NO_3^-	= 97.5 ppm	= 1.57 meq/l
HCO_3^-	= 82.5	= 1.35
Cl	= 95.9	= 2.70
$SO_4^=$	= 325	= 6.77
	Total Anion	12.39

BV(N) from Equation (13) = 150

BV(N) from Equation (14) = 156

Residual Nitrate on Exhausted Column - Step 2

Assume that a product water of 30-ppm (0.48 meq/l) nitrate is desired. The equivalent fraction of the column remaining in the nitrate form after regeneration and at start of run is estimated from Equation (2).

$$\frac{\overline{X'_N}}{1 - \overline{X'_N}} = K_C^N \frac{X_N}{1 - X_N}$$

$$\frac{\overline{X'_N}}{1 - X'_N} = 4 \times \frac{0.039}{1 - .039} = 0.162$$

$$\overline{X'_N} = 0.139$$

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Capacity of Partially Regenerated Column - Step 3

The capacity, BV(N)', of the partially regenerated column will be

$$BV(N)' = BV(N) \times (1 - 0.139)$$

$$= 150 \times .861 = 129$$

Regenerant Requirements - Step 4

Regeneration will remove all sulfate and reduce nitrate equivalent fraction on column to $\overline{X_N} = 0.139$. The amount of sulfate on the column at the end of the run is

$$[\overline{SO_4}] = \text{eq } SO_4^{=}/l \text{ on resin} = BV(N)' \times [SO_4^{=}] \times 10^{-3}$$

$$= 129 \times 6.77 \times 10^{-3}$$

$$= 0.873 \text{ eq/l}$$

The equivalent fraction of nitrate, $\overline{X_N}$, on the column at the end of the run is

$$\overline{X_N} = \frac{\text{meq } NO_3^-/l \text{ on resin} \times 10^{-3}}{\text{resin capacity (eq/l)}} = \frac{[\overline{NO_3}]}{1.3}$$

$$= \frac{BV(N)'}{1.3} \times ([NO_3^-] \text{ influent} - [NO_3^-] \text{ effluent}) \times 10^{-3} + \text{equivalent fraction of column in nitrate form at start of run}$$

$$= \frac{129}{1.3} \times (1.57 - .48) \times 10^{-3} + .139$$

$$= 0.247$$

The amount of sodium chloride regenerant required to remove the sulfate is estimated on the basis of 1 eq of NaCl required for each equivalent

of sulfate on the column. The amount of sodium chloride required for removal of sulfate from 1 cubic foot of resin is:

$$[\overline{SO_4}] \times 28.31 \text{ l/cu ft} = \text{eq NaCl/cu ft resin}$$

$$.873 \text{ eq/l} \times 28.31 \text{ l/cu ft} = 24.73 \text{ eq NaCl/cu ft resin}$$

$$\frac{24.73 \text{ eq NaCl/cu ft resin} \times 58.45 \text{ g/eq}}{454 \text{ g/lb}} = 3.18 \text{ lb NaCl/cu ft resin}$$

The amount of sodium chloride required to reduce $\overline{X_N}$ from 0.247 to 0.139 is estimated from Curve A of Figure 14 as 2.24 pounds of NaCl per cubic foot resin. The total regenerant requirement is 3.18 + 2.24 = 5.42 lb/cu ft resin.

The column will therefore treat 129 BV of Well 3 water and lower nitrate from 85 ppm to 30 ppm.

Regenerant requirements are then 5.42 pounds per (0.129 BV x 7.48) gallons = 5.62 pounds per 1,000 gallons of treated water. This can be compared to pilot column data for Well 3 shown in Figure 21 which shows, at 5.42 pounds of NaCl per cubic foot of resin, the approximate leakage of nitrate through the column is 30 ppm. Data shown in Table 12 (Runs 02270 through 03070A) also verifies the estimate of nitrate leakage through the column. For these runs, an average of 5.1 pounds of NaCl was used as regenerant, and the average leakage was 27.8 ppm. The BV treated by the incompletely regenerated pilot column, however, was less in each case than the estimated value of 129 BV. Bed volumes to breakthrough for all runs in Table 12 were determined at NO_3^- = 45 ppm thus making the value lower than that obtained if this point is determined at 1/2 x (influent NO_3^- effluent NO_3^-). The average sodium chloride regenerant requirement to reduce

Well 3 water to NO_3^- = 30 ppm for the above runs is 6.64 pounds per 1,000 gallons compared with the estimated 5.62 or 18 percent higher than the estimated value.

For lesser salt loadings listed in Table 12 (Runs 01220 to 02260), the average values obtained with the pilot column compared to the estimated values are:

	Average of Runs 01220 to 02260	Estimated
NO_3^- leakage ppm	44	45
Salt loading lb/cu ft	2.40	3.76
Bed volumes treated	68.5	112
Salt loading per 1,000 gallons of Well 3 treated	4.69	4.48

For higher salt loadings listed in Table 12 (Runs 03120 through 03210), the comparative values are:

	Average of Runs 03120 to 03210	Estimated
NO_3^- leakage ppm	22.5	22.5
Salt loading lb/cu ft	7.89	5.54
Bed volumes treated	121	134
Salt loading per 1,000 gallons Well 3 water	8.7	5.52

The discrepancy between the observed and estimated values for salt loading in this case can be attributed to the inefficiency of the regeneration process in the pilot column used coupled with the known difficulties of removing nitrate from resin where $\overline{X_N}$ is low.

ESTIMATES FOR McFARLAND WELL 2 AND OTHER WATERS

The above method is applied here to waters of other compositions to give product water of approximately 30 ppm in nitrate.

The McMWCo Well 2 has the following approximate composition:

NO_3^-	= 56.7 ppm	= 0.91 meq/l
HCO_3^-	= 71.9	= 1.18
Cl^-	= 60.5	= 1.70
$SO_4^=$	= 197	= 4.10
	Total Anion	= 7.89

Reduction of nitrate to 30 ppm would provide a water suitable for blending with an equal portion of raw water having a nitrate level below 60 ppm. Use of the above method to estimate the amount of regenerant to reduce nitrate at Well 2 gives the following values:

NO_3^- leakage (ppm)	= 30
Salt loading (lb/cu ft)	= 3.71
Bed volumes treated	= 199
Salt loading per 1,000 gallons Well 2 water treated (lb)	= 2.49
Salt requirement per 1,000 gallons blended water (lb)	= 1.25
Cost of regenerant per 1,000 gallons of blended water @ 1.5 cents per pound	= 1.88 cents

Comparative values of waters of various composition are given in Table 13.

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TABLE 13. REGENERATION REQUIREMENTS FOR WATERS OF VARIOUS COMPOSITIONS

Water Composition → / Operating Parameter ↓							
	NO_3^- meq/l	1	1	1.5	1.5	1.5	1.5
	HCO_3^-	1	1	1	1	1	1
	Cl^-	1	1	1	1	1	1
	$SO_4^=$	.5	3	3	2	1	.5
	Total Anion	3.5	6.0	6.5	5.5	4.5	4.0
NO_3^- in product water ppm		30	30	30	30	30	30
Bed volumes treated to breakthrough		423	229	207	247	307	347
Salt loading lb/cu ft		2.15	3.73	4.13	3.67	3.36	3.22
Salt requirement lb/1,000 gallons		0.68	2.18	2.67	1.98	1.46	1.24

The salt requirements for these waters appear remarkably low to those accustomed to thinking that ion exchange will generate large quantities of brine. These low values are made possible only by operation of an incompletely regenerated column from which nitrate can be removed by the regenerant at higher efficiency.

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SECTION 6

EQUIPMENT COST ESTIMATES FOR SINGLE COLUMN ION EXCHANGE SYSTEM

USE OF COMMERCIAL HARDNESS REMOVAL HARDWARE

Commercially available water softening systems are attractive as available pre-engineered hardware for nitrate removal applications. It appears such systems can be adapted for use as a conventional single column anion exchanger for nitrate removal. Some modifications and substitution of a strong base anion exchange resin must be made to adapt those systems to nitrate removal by a single column ion exchange process. Sizing of single column ion exchange systems can be based on the above pilot column tests to treat well water by conventional ion exchange processing. By "single column" is meant passage of the water to be treated through an ion exchange bed composed of one resin type until the exchange resin is exhausted. The column is then removed from service and regenerated with sodium chloride brine in downflow mode. During regeneration of the column, a second ion exchange column is put into service. As shown in Section 4, a regeneration load in excess of 20 pounds NaCl per cubic foot of resin is required to remove all nitrate from an exhausted column. However, some nitrate can remain on the column if a product water with less than 45-ppm nitrate is acceptable thus reducing the salt requirement considerably.

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The primary equipment required is a resin tank equipped with a flow distributor for introduction of raw water and removal of backwash water. A second flow distributor should be installed to introduce regeneration brine near the upper surface of the resin bed. A filter system at the bottom of the resin tank supports the resin and collects the treated water. Tanks for storage of salt and brine are also required.

Brine can either be pumped or educted from the brine tank, mixed with untreated water, and allowed to pass through the brine distributor through the resin and then to waste. Brine is passed downflow through the resin.

After exhaustion of the anion exchange resin, nitrate will be concentrated at the bottom of the column due to chromatographic separation of sulfate and nitrate. In downflow regeneration, the nitrate is thus ideally closest to the exit end of the column and need not be moved by the regenerant through the entire bed. After regeneration, any nitrate remaining on the column will also be concentrated at the base of the column. This will require declassification (mixing to form a homogeneous resin composition throughout the column) of the resin before it is put back into service. Because of these characteristics, the service cycle should be followed by brine rinse and then backwashing and/or declassification.

Column operation is easily automated making labor requirements minimal. The regeneration cycle can be initiated by an integrating flowmeter on the treated water stream. Ideally, continuous nitrate monitoring with automatic alarm and control system should be employed. The backwash and regeneration periods are controlled by a single timer which controls the flow of processing water through the systems' values.

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Upflow regeneration of a resin column can also be used to give an effluent of very low nitrate in treated water and thereby making blending possible. This is due to the complete regeneration of resin in the lower portion of the column leaving the nitrate residue at the top of the column. This method of regeneration is being investigated on this program and, if found to be successful, it will reduce the cost of water produced by reducing the size of the equipment required for treatment. The costs and production parameters are estimated below using conventional downflow regeneration.

SIZING OF CONVENTIONAL SINGLE COLUMN ION EXCHANGE SYSTEMS

The columns are sized to treat water pumped directly from a well through the ion exchange columns into a surge tank serving the municipal water system. Two columns can be provided for "one-on/one-off" operation to allow continuous service while one column is regenerated.

Resin Quantity - Tank Size

Well water production rate mgd	1.0
gpm	694
Fraction of well water treated by ion exchange	1.0
Volume to be exchanged gpm (avg)	694
at maximum pump rate gpm	907
Minimum volume of resin on stream at 20 gpm/ft^2; 36-inch bed depth 6.67 gpm/ft^3; ft^3	136
Tank size diameter inches	91.2
height inches	60
Use two available tanks diameter inch	72
height inch	60
Resin volume, ft^3	169

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Factors Applicable to Well 3 - McFarland

Treated water NO_3^- level ppm		30
Estimated capacity, Per cycle	BV	129
	gallons	163,000
Time for exhaustion	minutes	180
	hours	3.0
Brine rinse ca 1.5 BV of 6%; min (gal)		15 (1,896)
Slow rinse 3.5 BV; min (gal)		45 (4,424)
Backwash 5 gal/ft^2 resin area/min (recyclable); min (gal)		10 (3,000)
Time for regeneration cycle, min		70
Wastewater gallons per cycle		6,320
	BV	4.9
	gpd (peak)	50,560
	gpd (average)	38,686

COST OF COMMERCIAL ION EXCHANGE SYSTEMS

Systems for Treating Total Well Production

A commercially available system suitable for treating all water from a 1-mgd producing well for nitrate removal involves the following equipment costs. These costs are based on single column operation employing a pair of 72-inch-diameter resin tanks containing 136 cubic feet of resin. A second pair of resin tanks is included in the cost to allow continuous operation of the well while one pair of the resin tanks is in the regeneration cycle.

Costs are estimated based on GSA pricing f.o.b. at the factory.

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4	Fabricated resin tanks 72" x 60" (including valves, electrical controls, and flow distributors)	$ 66,234
2	Alternators	640
2	4-Inch reset meters	4,893
4	Solenoid kits	122
1	Brine pump	416
1	40-Ton brine maker (including level controls sight glasses)	15,430
1	Air injector	2,000
338	Cubic feet resin @ $150/cu ft	50,700
	Plumbing installation	2,000
	Concrete pad 25 x 15	2,000
	Startup and loading by vendor	1,000
	TOTAL	$145,435

Systems for Treating One-Half of Well Production

A system for treating one-half of the production of a 1-mgd producing well is useful where nitrate level can be reduced to a level to make blending with untreated water possible. For example, treatment of McFarland Well 2 can reduce nitrate to 30 ppm. This product water can be blended with an equal volume of untreated water to give a blended water where nitrate is less than 45 ppm.

Resin Quantity - Tank Size

Well water production rate mgd	1.0
gpm	694
Fraction of well water treated by ion exchange	0.5
Volume to be exchanged gpm (avg)	347
at maximum pump rate gpm	454
Minimum volume of resin on stream at 20 gpm/ft^2; 36-inch bed depth, cu ft 6.67 gpm/ft^3; ft^3	68
Tank size diameter inches	64
height inches	60
Use available tank diameter inch	72
height inch	60
Resin volume, ft^3	85

Factors Applicable to Well 2 - McFarland

Treated Water NO_3^- level ppm		30
Estimated capacity, Per cycle	BV	199
	gallons	126,524
Time for exhaustion	minutes	279
	hours	4.65
Brine rinse ca 1.33 BV of 6% NaCl; min (gal)		15 (846)
Slow rinse 3.5 BV; min (gal)		45 (2,225)
Backwash 5 gal/ft^2 resin area; min (gal) (recyclable); min (gal)		10 (1,400)
Time for regeneration cycle, min		70
Wastewater gallons per cycle		3,071
	BV	4.83
	gpd (peak)	15,850
	gpd (average)	12,114

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Capital Equipment Cost

2	Fabricated resin tanks 72" x 60" (including valves, electrical controls, and flow distributors)	$33,117
2	Alternators	640
2	4-Inch reset meters	4,893
4	Solenoid kits	122
1	Brine pump	416
1	40-Ton brine maker 10' x 14' 6" (including level controls sight glasses)	15,430
1	Air injector	2,000
170	Cubic feet resin @ $150/cu ft	25,500
	Plumbing installation	2,000
	Concrete pad	2,000
	Startup and loading by vendor	1,000
	TOTAL	$86,818

SECTION 7

REVERSE OSMOSIS EXPERIMENTS

SINGLE MODULE REVERSE OSMOSIS SYSTEM

Two R.O. systems are being used for nitrate removal studies. A single module system allows for testing of individual R.O. membrane modules on various feed waters. Feed water is mixed in a 150-gallon tank from which it is pumped to feed a high pressure pump capable of delivering 10 gpm at up to 450 pounds per square inch. This pressurized feed water is pumped through the brine channels of the selected membrane module. Product and feed water streams are sampled and then either discarded or recombined in the feed tank.

A series of experiments was run comparing the performance of five different single R.O. modules. Feed water from Well 3 was treated with sulfuric acid to adjust the pH to 4.1. The water was not chlorinated. Each R.O. module was operated in the single module R.O. loop system for one to two hours before data was taken. Data on nitrate and sulfate removal are given in Table 14. The best overall performance was obtained with the DuPont B-9 module giving high water recovery.

PILOT PLANT REVERSE OSMOSIS SYSTEM

A pilot plant R.O. system was installed on the pad at Well 3. The plant has a production capacity of 14 gpm (ca 20,000 gallons per day) with cellulose acetate spiral wound membranes. Operating data for the plant is as follows:

TABLE 14. COMPARISON OF R.O. MEMBRANE TYPES ON McFARLAND WELL 3 WATER

Membrane I.D.	Type	% Water Recovery Per Single Module	Feed Pressure	Product (ppm) NO_3^-	Product (ppm) $SO_4^=$	Product (ppm) TDS[≠]	Brine (ppm) NO_3^-	Brine (ppm) $SO_4^=$	Brine (ppm) TDS[≠]
PA-300	SP[a]	34	400	20.2	21	75	145.2	455	925
CA-HP[b]	SP[a]	24	395	32.6	2	50	132.0	480	900
CA-LP[c]	SP[a]	17	200	77.4	44	255	112.6	445	825
Dowex R.O. 25	HF[d]	4.5	200	26.4	4	50	110.0	400	780
DuPont B-9	HF[d]	52	310	8.8	2	25	189.2	600	1,175

[a] SP = Spiral wound.
[b] CA-HP = Cellulose acetate high pressure.
[c] CA-LP = Cellulose acetate low pressure.
[d] HF = Hollow fiber.

Feed water composition ppm:

NO_3^- = 105.6; Cl_2 = 0

$SO_4^=$ = 365

TDS[≠] = 750

pH = 4.1

[≠] TDS = Measured by R.O. meter

Operating Data:

Number of elements (total)	18
Stage 1	12
Stage 2	6
Operating temperature	70° F
Nominal flow (gpm) for:	
Product	13.9 gpm
Feed	18.5
Reject	4.6
Overall plant conversion (recovery)	75 percent
Salt rejection*	92.5 to 94.5 percent
Feed operating pressure (nominal)	400 psig

*Nominal rejection based on 2,000-ppm NaCl solution at 420-psig operating feed pressure, 10 percent water recovery, and 77° F operating temperature.

Several mechanical and electrical problems have been encountered in operating the system to date. Limited operating data after the first 100 hours of operation have been obtained as follows:

Constituent	Well 3[a] (ppm)	R.O. Product[b] (ppm)	R.O. Brine[b] (ppm)
Ca	154	7.0	590
Mg	3.8	0.16	15
Na	92	11	345
Cl^-	92.8	6.0	347
$SO_4^=$	380	5	1,500
NO_3^-	93.0	31.9	270
TDS	823	64	2,900

[a] After pretreatment.
[b] Water recovery 73.9 percent.

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2. D. A. Clifford and W. J. Weber, "Nitrate Removal From Water Supplies by Ion Exchange," EPA-600/2-78-052, June 1978.

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